



THE  
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# PROCEEDINGS AT THE MEETINGS OF THE PHYSICAL SOCIETY

SESSION 1928-1929

*Except where the contrary is stated, the meetings were held at the Imperial College of Science and Technology, South Kensington.*

October 26, 1928.

W. H. ECCLES, D.Sc., F.R.S., and subsequently R. W. PAUL, in the Chair.

1. A paper entitled, "An Experimental Study of the Anticlastic Bending of Rectangular Bars of Different Cross-Sections," by ALLAN FERGUSON, M.A., D.Sc., and JAS. P. ANDREWS, M.Sc., was read by Mr Andrews.

2. A paper entitled, "An Instrument for the Production of Known Small High-Frequency Alternating Electromotive Forces," by B. S. SMITH, A.M.I.E.E., F.Inst.P., and F. D. SMITH, M.Sc., A.M.I.E.E., was read by Mr F. D. Smith.

3. A demonstration of a New Device for Thermostatic Control was given by H. F. T. JARVIS, B.Sc., Birkbeck College.

November 9, 1928.

W. H. ECCLES, D.Sc., F.R.S., in the Chair.

1. The following were elected Fellows of the Physical Society: Har Chand Singh, Arthur Ernest Bate, Stanley Whitehead, Satyendra Ray, Louis Cohen, Dorothy Lilian Tilleard, Rupert Henry Saunders, Horace Pearson Walmsley.

The President announced that the Council had elected the following Student Members of the Society: Leslie Charles Bailey, Reginald Frederick Clark, Arthur William Carter, Morris Lazarus Savronsky, Sidney John Kennedy, Leonard Francis Osmond, Harry James Shepherd, John Guyscliffe Holmes, Basil Gordon Dickins, Wilfrid Basil Mann.

2. A paper entitled, "The Effect of Moist Air on the Resistance of Pencil Lines," by J. B. SETH, M.A., CHETAN ANAND, M.A., and GIAN CHAND, M.Sc., was read by Dr Allan Ferguson in the absence of the authors.

3. A paper entitled, "An Absolute Current-balance having a Simple Approximate Theory," by L. F. RICHARDSON, D.Sc., F.R.S., V. STANYON, B.Sc., and other Students of Westminster Training College was read by Dr Richardson, and a demonstration of the apparatus described was given by Messrs V. STANYON, B.Sc., and G. W. ROE, B.Sc.

4. A paper entitled, "Notes on Wireless Methods of Investigating the Electrical Structure of the Upper Atmosphere," was read by E. V. APPLETON, F.R.S.

## *Proceedings*

*November 23, 1928.*

W. H. ECCLES, D.Sc., F.R.S., in the Chair.

1. The following were elected Fellows of the Physical Society: Leslie Martin Clark, Joseph Parker Manickasingham, C. A. Luxford.

The President announced that the Council had elected the following Student Members of the Society: Sidney Jefferson, Ronald Curry.

2. A paper entitled, "The Effect of Superimposed Magnetic Fields on Dielectric Losses and Electric Breakdown Strength," by ALLAN MONKHOUSE, M.I.E.E., A.M.I.Mech.E., was taken as read, in the absence of the author.

3. A paper entitled, "A New A.C. Potentiometer of Larsen Type," was read by ALBERT CAMPBELL, M.A.

4. A paper entitled, "Ferromagnetic Ferric Oxide," was read by Prof. E. F. HERROUN, F.I.C., and Prof. E. WILSON, M.Inst.C.E., M.I.E.E.

5. A paper entitled, "The Physical Interpretation of Wave Mechanics," was read by G. TEMPLE, Ph.D., 1851 Exhibition Research Student, Imperial College of Science.

6. A demonstration of Emulsions showing Chromatic Effects was given by R. H. HUMPHRY, M.Sc., The Sir John Cass Technical Institute.

*December 14, 1928.*

W. H. ECCLES, D.Sc., F.R.S., in the Chair.

1. The following were elected Fellows of the Physical Society: Teresa Joseph Dillon, Frederick Robert Charles Rouse, Robert Constantine Graseby, L. G. Vedy.

The President announced that the Council had elected the following Student Members of the Society: Godfrey Henry Barker, Lionel V. Cole, Arnold Joseph Holland, R. Jessel.

2. A lecture entitled, "A Survey of Heat Conduction Problems," was given by EZER GRIFFITHS, D.Sc., F.R.S., and was followed by a discussion.

*January 8, 9 and 10, 1929.*

The Nineteenth Annual Exhibition of the Physical Society and the Optical Society was held in the Imperial College of Science.

Discourses were delivered as follows:

*January 8th:* Prof. F. LLOYD HOPWOOD, D.Sc., F.Inst.P., "Experiments with High-Frequency Sound Waves."

Mr S. R. HUMBY, "Some Experiments with Sound Waves."

*January 9th:* Mr CONRAD BECK, C.B.E., "Lenses."

Mr S. R. HUMBY, "Some Experiments with Sound Waves."

*January 10th:* Mr A. J. BULL, M.Sc., F.Inst.P., "Some Colour Problems in Photo-Engraving."

*January 25, 1929.*

W. H. ECCLES, D.Sc., F.R.S., in the Chair.

1. The following was elected a Fellow of the Physical Society: Thomas Logie MacDonald.

The President announced that the Council had elected the following a Student Member of the Society: Alastair Watson Gillies.

2. A paper entitled, "A Fused Quartz Pendulum Rod for Clocks," was read by Prof. C. VERNON BOYS, F.R.S.

3. A paper entitled, "A Method for the Determination of the Equivalent Resistance of Air-Condensers at High Frequencies," was read by G. W. SUTTON, B.Sc.

4. A paper entitled, "The Measurement of the Anode Circuit Impedances and Mutual Conductances of Thermionic Valves," was read by L. HARTSHORN, A.R.C.S., B.Sc., D.I.C., The National Physical Laboratory.

*February 8, 1929.*

W. H. ECCLES, D.Sc., F.R.S., in the Chair.

1. The following were elected Fellows of the Physical Society: Kenneth Drinkall, Edwin Irving Harrison, Heinrich Richard Ronnebeck, Owen Alfred Saunders, F. J. M. Stratton, Reginald Alfred Fereday, William Singleton, R. W. B. Pearse, William Edward Pretty.

2. A paper entitled, "The Photographic Measurement of the Relative Intensities of the  $L\alpha_1$ ,  $L\alpha_2$ ,  $L\alpha_3$  lines of Silver," was read by H. C. WEBSTER, M.Sc., Dixon Research Scholar, Natural Philosophy Laboratory, University of Melbourne.

3. A paper entitled, "Spark Satellites of the  $L\alpha$  lines of Silver," was read by H. C. WEBSTER, M.Sc., Dixon Research Scholar, Natural Philosophy Laboratory, University of Melbourne.

4. A demonstration of a new instrument for the rapid and accurate determinations of the specific gravities of solid substances was given by Mr W. A. BENTON, Head of the Research Department, Messrs W. and T. Avery, Ltd.

*February 22, 1929.*

D. OWEN, B.A., D.Sc., in the Chair.

1. The following was elected a Fellow of the Physical Society: Alfred Charles Hiscocks.

2. A paper entitled, "The Construction and Calibration of a Sensitive Form of Pirani Gauge for the Measurement of High Vacua," was read by L. F. STANLEY, A.R.C.S., B.Sc., Research Student, The Royal College of Science.

3. A paper entitled, "The Free Periods of a Composite Elastic Column or Composite Stretched Wire," was read by CHARLES H. LEES, D.Sc., F.R.S.

4. A paper entitled, "A Capillary Tube Method for the Simultaneous Determination of Surface Tension and of Density," was read by ALLAN FERGUSON, M.A., D.Sc., and J. A. HAKES, B.Sc.

5. A demonstration of a standard electrostatic voltmeter and wattmeter, used for measurements of alternating currents at power frequencies at the National Physical Laboratory, was given by Dr E. H. RAYNER.

*March 8, 1929.*

W. H. ECCLES, D.Sc., F.R.S., in the Chair.

1. The following were elected Fellows of the Physical Society: James Allan Hakes, Edgar Isaac Everett, Robert Edward Herrick.

The President announced that the Council had elected the following a Student Member of the Society: Richard Leonard Ascough Borrow.

2. A paper entitled, "The Dependence of the Mobility of Ions in Air on the Relative Humidity," by EZER GRIFFITHS, D.Sc., F.R.S., and J. H. AWBERY, B.A., B.Sc., was read by Dr EZER GRIFFITHS.

3. A paper entitled, "Some Unsolved Problems relating to the Mobilities of Gaseous Ions," was read by Prof. A. M. TYNDALL, D.Sc.

4. The reading of the above papers was followed by a general discussion on the mobility of ions, in which the following took part: Messrs J. H. Awbery, C. F. Powell, S. P. MacCallum, L. G. H. Huxley, D. Owen, J. H. Vincent, F. J. W. Whipple, and (by communication) K. L. Goodall.

*Annual General Meeting, March 22, 1929.*

W. H. ECCLES, D.Sc., F.R.S., in the Chair.

1. The reports of the Council and Hon. Treasurer were presented and adopted.

2. Dr W. JEVONS and Dr E. G. RICHARDSON having been appointed scrutators, the following officers and members of Council were elected unanimously for 1929-1930:

*President:* W. H. Eccles, D.Sc., F.R.S.

*Vice-Presidents (who have filled the office of President):* Sir Oliver J. Lodge, D.Sc., F.R.S.; Sir Richard Glazebrook, K.C.B., D.Sc., F.R.S.; Prof. H. L. Callendar, M.A., LL.D., F.R.S.; Sir Arthur Schuster, Ph.D., Sc.D., F.R.S.; Sir J. J. Thomson, O.M., D.Sc., F.R.S.; Prof. C. Vernon Boys, F.R.S.; Prof. C. H. Lees, D.Sc., F.R.S.; Prof. Sir W. H. Bragg, K.B.E., M.A., F.R.S.; Alexander Russell, M.A.,

D.Sc., F.R.S.; F. E. Smith, C.B., C.B.E., D.Sc., F.R.S.; Prof. O. W. Richardson, M.A., D.Sc., F.R.S.

*Vice-Presidents:* R. W. Paul; J. S. G. Thomas, D.Sc.; Prof. A. O. Rankine, O.B.E., D.Sc.; Prof. F. L. Hopwood, D.Sc.

*Hon. Secretaries:* Ezer Griffiths, D.Sc., F.R.S.; Allan Ferguson, M.A., D.Sc.

*Hon. Foreign Secretary:* Prof. O. W. Richardson, M.A., D.Sc., F.R.S.

*Hon. Treasurer:* R. S. Whipple.

*Hon. Librarian:* J. H. Brinkworth, M.Sc., A.R.C.S.

*Ordinary Members of Council:* Miss A. C. Davies, D.Sc.; Prof. A. M. Tyndall, D.Sc.; T. Smith, M.A.; J. Guild, A.R.C.S., D.I.C.; Prof. W. Wilson, Ph.D., D.Sc., F.R.S.; D. Owen, B.A., D.Sc.; Sir Richard Paget, Bart.; Major I. O. Griffith, M.A.; D. W. Dye, D.Sc., F.R.S.; A. B. Wood, D.Sc.

3. Prof. PIETER ZEEMAN was unanimously elected an Honorary Fellow of the Society.

4. A vote of thanks to the honorary auditors, Mr L. Hartshorn and Dr E. H. Rayner, was proposed by Dr J. S. G. THOMAS, seconded by Mr T. SMITH, and carried by acclamation.

5. A vote of thanks to the retiring officers and Council was proposed by Dr S. MARSH and seconded by Dr W. S. TUCKER. It was mentioned that special reference was made to the retirement of Prof. A. O. RANKINE from the post of Hon. Secretary (Business), which he had filled with great advantage to the Society for  $5\frac{1}{2}$  years. The vote was carried by acclamation.

6. A vote of thanks to the Governors of the Imperial College of Science, for permitting the Society to use the College buildings, was proposed by Dr D. OWEN, seconded by Mr R. S. WHIPPLE, and carried by acclamation.

*Ordinary Meeting following the Annual General Meeting.*

W. H. ECCLES, D.Sc., F.R.S., in the Chair.

1. The following were elected Fellows of the Physical Society: H. J. E. Bailey, G. M. B. Dobson, T. C. Keeley.

2. The Presidential Address was delivered by Dr W. H. ECCLES, F.R.S., who took as his subject: "The New Acoustics."

A vote of thanks to the lecturer was proposed by Prof. F. L. HOPWOOD, seconded by Mr R. W. PAUL, and carried by acclamation.

*April 19, 1929.*

W. H. ECCLES, D.Sc., F.R.S., in the Chair.

1. The following was elected a Fellow of the Physical Society: Donald McKerracher.

2. The Duddell Medal for 1928 was presented to Dr C. E. GUILLAUME who, after expressing his thanks, briefly explained some aspects of his work.

3. The Fourteenth Guthrie Lecture was delivered by Prof. P. W. BRIDGMAN, Hollis Professor of Mathematics and Natural Philosophy in Harvard University, on the Properties of the Elements under High Pressures.

A vote of thanks to the lecturer was moved by Sir ROBERT A. HADFIELD, F.R.S., seconded by Prof. A. W. PORTER, F.R.S., and carried by acclamation.

*April 26, 1929.*

Prof. F. L. HOPWOOD, D.Sc., in the Chair.

1. The following was elected a Fellow of the Physical Society: G. P. Barnard.

2. A discussion on the Teaching of Geometrical Optics was held.

At the close of the discussion Mr T. SMITH suggested that the Council of the Physical Society should be requested to take steps for the appointment of a committee, comprising a small number of representatives of the Society and of appropriate organisations of teachers, for the purpose of giving effect to the conclusions arising out of the discussion. This proposal was agreed to unanimously.

*May 10, 1929.*

W. H. ECCLES, D.Sc., F.R.S., in the Chair.

1. A paper entitled, "Heaviside's Fractional Differentiator," by W. E. SUMPNER, D.Sc., M.I.E.E., was taken as read in the absence of the author.

2. A paper entitled, "A Simple Method of Fitting a Straight Line to a Series of Observations," was read by J. H. AWBERRY, B.A., B.Sc., Physics Department, The National Physical Laboratory.

3. A paper entitled, "Arc Spectra in the Region  $\lambda$  1600- $\lambda$  2100," was read by E. W. H. SELWYN, B.Sc.

4. A paper entitled, "The Spectrum of Trebly-ionised Thallium," was read by K. R. RAO, D.Sc., Imperial College of Science.

5. A paper entitled, "The Elastic Properties of Thick Cylindrical Shells under Internal Pressure," was read by G. A. WEDGWOOD.

6. A demonstration relating to Standards of Length and Mass was given by J. E. SEARS, C.B.E., The National Physical Laboratory.

*May 14, 1929.*

*Meeting held jointly with the Society of Glass Technology at the Research Laboratories of the General Electric Company, Ltd., Wembley.*

W. H. ECCLES, D.Sc., F.R.S., in the Chair.

The following papers were read:

1. "A Study of the Thermal Expansion of Glass up to the Softening Temperature," by Prof. W. E. S. TURNER, O.B.E., D.Sc., F.Inst.P., and F. WINKS, M.Sc.Tech.
2. "The Measurement of the Viscosity of Glass at High Temperatures by means of the Rotating Cylinder Viscometer," by R. F. PROCTOR, B.Sc., A.M.I.E.E., and R. W. DOUGLAS. (A communication from the Staff of the Research Laboratories of the General Electric Co., Ltd., Wembley.)
3. "The Photo-Elastic Properties of Glass," by F. C. HARRIS, M.Sc., Department of Applied Mathematics, University College, London.

The Research Laboratories of the General Electric Co., Ltd., at Wembley, were inspected by Fellows before the meeting.

After the meeting the Glass Works of the Osram General Electric Company were visited, by courtesy of the Manager, Mr W. WARREN, A.M.I.C.E., A.M.I.E.E.

*May 24, 1929.*

W. H. ECCLES, D.Sc., F.R.S., in the Chair.

1. The following were elected Fellows of the Physical Society: Philip E. Belas, William Bergin, George William Brindley, Alexander Morris Cassie, James Gerald Crowther, E. J. Evans, Arthur Eric Knowler, Wilfred Llowarch, A. R. Marshall, Kenneth Emerson Pattinson, Harold Norman Pighills, George Gibson Sherratt, William Griffiths Tonner, Frank Andrews Walker.
2. A paper entitled, "A Hygrometer for use in Timber-Seasoning Kilns," was read by EZER GRIFFITHS, D.Sc., F.R.S., Physics Department, National Physical Laboratory, Teddington, Middlesex.
3. A paper entitled, "Experiments on Magnetostrictive Oscillators at Radio Frequencies," was read by J. H. VINCENT, M.A., D.Sc., F.Inst.P.
4. A demonstration of an apparatus for measuring the Thermal Expansion of Glass was given by F. WINKS, M.Sc.Tech.
5. A demonstration of the Flutter of Model Aeroplane Wings was given by W. J. DUNCAN, The National Physical Laboratory.



*June 14, 1929.*

W. H. ECCLES, D.Sc., F.R.S., and subsequently R. W. PAUL, in the Chair.

1. The following were elected Fellows of the Physical Society: L. F. G. SIMMONS, Parmeshwar Dayal.

2. A paper entitled, "The Zeeman Effect for the Arc Spectrum of Gold," by A. S. M. SYMONS, A.R.C.S., D.I.C., B.Sc., and J. DALEY, A.R.C.S., D.I.C., B.Sc., was taken as read in the absence of the authors.

3. A paper entitled, "The Band Spectrum of Lanthanum Monoxide," preceded by a Note on Electronic Band Spectra of Diatomic Molecules, was read by W. JEVONS, D.Sc., F.Inst.P.

4. A paper entitled, "Pressure Shifts in Line Spectra of Gases," was read by W. E. PRETTY, A.R.C.S., D.I.C., B.Sc., The Imperial College of Science.

5. Exhibits showing the Crystal Structure of Manganese and Aluminium Alloys were shown by G. D. PRESTON, B.A.

*June 28, 1929.*

1. The following were elected Fellows of the Physical Society: Frederick F. P. BISACRE, M.A., B.Sc., Thomas W. MINETT, B.Sc., Edmund Clifton Stoner.

2. A demonstration of some Contact Devices used in an Apparatus for the Measurement of Electrical Resistance at High Temperatures was given by J. L. HAUGHTON, D.Sc., of the National Physical Laboratory.

3. A paper entitled, "The Relation between Hydrogen Pressure and Filament Resistance in a Tube containing Glowing Tungsten," was read by TERESA J. DILLON, B.Sc., Ph.D., London School of Medicine for Women.

4. A paper entitled, "The Band Systems of Titanium Oxide," was read by FRANCES LOWATER, Ph.D., F.R.A.S.

5. A paper entitled, "The Absolute Measurement of Sound Intensity," was read by F. D. SMITH, M.Sc., Admiralty Research Laboratory, Teddington.

*Visit to Birmingham, July 6, 1929.*

On arrival at Leamington the visitors drove by motor-bus, provided by the University, to Birmingham via Warwick. At Warwick a stop was made to enable members to inspect Warwick Castle and other places of historic interest. Lunch was served about 1.30 p.m. at the University Refectory in the Edgbaston Buildings, and thereafter the University Science Buildings were open to inspection.

A demonstration was given at 2.30 p.m. in the Mechanical Engineering Department by Prof. F. W. BURSTALL, Vice-Principal of the University.

A Meeting of the Society was held at 3 p.m., Prof. F. L. HOPWOOD being in the Chair. Tea was taken at 4.30 p.m. in the Physics Block, and was followed by demonstrations and an exhibition of apparatus in the Physics Department.

At the meeting the following papers were read in abstract:

"The Magnetic Analysis of Steels," by S. W. J. SMITH, M.A., D.Sc., F.R.S., and A. A. DEE, B.Sc., D.I.C.

"Thermal Diffusion at Low Temperatures," by T. L. IBBS, M.C., Ph.D., and K. E. GREW, B.Sc.

"The Damping of Vibrations in Steel Tuning Forks and its Variation with Temperature," by G. BARLOW, D.Sc., and H. B. KEENE, D.Sc.

"The Crystal Structure of some Carbohydrates," by J. YOUNG, B.Sc., A.R.C.S.

"Note on the Origin of Certain Interatomic Forces," by M. C. JOHNSON, M.A., M.Sc.

The following demonstrations were given:

"A Micro-Hygrometer," by Dr G. A. SHAKESPEAR.

"Rainbow Jets," by Dr G. BARLOW.

"Etch Figures on Single Crystals of Nickel-Iron," by A. A. DEE.

"A Micro-Manometer," by M. C. JOHNSON and G. O. HARRISON.

and in the Mechanical Engineering Department:

(1) "Generation of Screw Threads"; (2) "Air Cooling"; by Prof. F. W. BURSTALL, Vice-Principal.

Some examples of the equipment of the Physical Laboratories for teaching purposes were shown also.

On behalf of the visitors a hearty vote of thanks to Prof. S. W. J. SMITH and his colleagues and to the University authorities was proposed by Dr J. H. VINCENT and carried by acclamation.

## REPORT OF THE COUNCIL FOR THE YEAR 1928

### *Meetings*

DURING the year fourteen Ordinary Science Meetings were held at the Imperial College of Science. At these meetings 33 Papers were presented and 10 Demonstrations given. By the kind invitation of Prof. Tyndall about 75 Members of the Society and their friends visited Bristol on July 7. The new University buildings were open for inspection and a Science Meeting was held in the Henry Herbert Wills Physical Laboratory, when several papers were read and demonstrations given by workers in the Laboratory.

Prof. Sir Joseph Thomson, O.M., F.R.S., delivered the Thirteenth Guthrie Lecture on March 9, the subject being "Electrodeless Discharges through Gases." About 280 Fellows and Visitors were present.

On December 14 Dr Ezer Griffiths, F.R.S., gave a lecture entitled "A Survey of Heat Conduction Problems."

The average attendance at meetings of the Society was 67.

### *Eighteenth Annual Exhibition*

The Eighteenth Annual Exhibition, arranged jointly by the Physical and Optical Societies, was held, through the courtesy of the Governing Body, at the Imperial College on January 10, 11 and 12. Trade exhibits were arranged by eighty-one firms, and the Research and Experimental Section contained exhibits contributed from twenty-three sources. Discourses were given by Mr A. Whitaker on "Progress in the Recording and Reproduction of Sound"; by Mr V. E. A. Pullin on "Recent Applications of X-rays"; and by Dr J. W. T. Walsh on "Artificial Daylight." On the third day the general public were admitted, and on the morning of January 11 a new special session was instituted, limited to members of the Physical and Optical Societies. The total attendance at the Exhibition was estimated at about 5000.

### *Officers*

During the early part of the year the Librarian, Mr J. H. Brinkworth, acted also as Business Secretary while Prof. A. O. Rankine was absent in Persia. Shortly after the Annual General Meeting on March 23 the Council received and accepted with much regret Mr J. Guild's resignation as Papers Secretary, placing on record their appreciation of his long and valuable services. Dr Allan Ferguson was appointed to succeed Mr Guild.

### *Representatives on Other Bodies*

Dr J. H. Vincent and Dr A. Ferguson have been appointed as representatives of the Society on the Board of the Institute of Physics; and Dr D. Owen and Dr A. Ferguson on the Science Abstracts Committee. Mr J. H. Brinkworth and Prof. A. O. Rankine have been appointed as representatives of the Society on a Joint Library Committee with the Institute of Physics and the Optical Society with a view to establishing a Physics Library at 1 Lowther Gardens.

Prof. A. O. Rankine represented the Society at the Centenary celebrations of the Institution of Civil Engineers in June and presented an address of congratulation on behalf of the Society. Prof. C. G. Darwin was the delegate of the Society at the Bologna meeting of the International Congress of Mathematicians in September.

*Honorary Fellow*

At the Annual General Meeting on March 23 Prof. Albert Einstein was unanimously elected an Honorary Fellow of the Society.

*Award of the Duddell Medal*

At the Annual General Meeting the Fifth (1927) Duddell Medal was presented to Dr F. E. Smith, F.R.S. The Council has awarded the Sixth (1928) Duddell Medal to Dr C. E. Guillaume, Honorary Fellow of the Society. The date of presentation is expected to be April 19, 1929.

*Fellows of Long Standing. Remission of Subscriptions*

On January 27 the Council passed unanimously the following resolution:

"Any Fellow having reached the age of 65, and having retired from the practice of his profession or business, may apply to the Council to remit or reduce his future annual subscriptions, provided his Fellowship of the Society has been continuous for at least 25 years. If his request be granted, he may nevertheless be required to pay, at a rate to be determined by the Council from time to time, for such publications of the Society as he may wish to receive."

In order to enable the Council to act upon this resolution an amendment was proposed to the Articles of Association which was duly adopted at Special General Meetings held on May 25 and June 8. Article 37 was thus amended by the addition of the words, "The Council may, however, in its discretion, reduce or remit the subscription of any individual Fellow, in special circumstances."

*Gifts to the Society*

The Council is indebted to Mr R. W. Paul for the gift of five bookcases for the Society's library, for use at 1 Lowther Gardens.

During the year the Council received a gift of about 100 parts of the Proceedings from Mr A. P. Trotter. These have been used as far as possible to institute a retrospective exchange back to 1899 with the Académie Royale de Belgique.

*New Publishing Arrangements*

As intimated in the last Annual Report the Cambridge University Press commenced printing the Proceedings and other publications of the Society in October, in relation to Volume 41. The fact that the Cambridge University Press did not wish to act as publishers necessitated a modification of the arrangement with the Institute of Physics referred to in the last Report. According to the new arrangement which the Council has made, the Institute has undertaken the publication of the Proceedings of the Society from 1 Lowther Gardens, and Mr Thomas Martin, the Secretary of the Institute, has been appointed Assistant Secretary of the Physical Society. Capt. C. W. Hume's title has accordingly been changed to Assistant Secretary (Editing).

As a result of the labours of the Publications Sub-committee, which completed its work and was dissolved on June 22, several important changes have been introduced which have resulted in speeding up publication, improving its production and reducing its net cost. The changes made involve the introduction of suitable advertisements and

## *Report of the Council for 1928*

reviews into the Proceedings, and the issue of the Bulletin in a duplicate form whereby on the one hand the issue of notices of meetings takes place more promptly, and on the other hand discussions of papers are recorded more accurately.

### *Obituary*

The Council records with deep regret the deaths of two Honorary Fellows, Prof. H. A. Lorentz and Prof. Willy Wien. Prof. Lorentz was the senior Honorary Fellow, having been elected in 1902. Prof. Wien was elected in 1925, and delivered the Guthrie Lecture in the same year. The Society has sustained another great loss in the death of Dr C. Chree, who was elected in 1896 and was President in 1908-10.

Other losses by death which the Council has with regret to record are: Rev. C. W. Bourne (elected 1874 during the first session of the Society), Mr A. Siemens (elected 1899), Mr W. H. Sodeau (elected 1896), Mr W. B. Croft (elected 1890 and served later on Council), Mr F. W. Shurlock (elected 1895), Mr H. Davey (elected 1891), Mr R. E. Day (elected 1875), Sir Horace Darwin (elected 1898), Mr W. Claude Johnson (elected 1889), all Life Fellows of the Society; also Mr H. Morris Airey (elected 1911).

### *Membership Roll*

The number of Honorary Fellows on the Roll on December 31, 1928 was 10. At the same date Ordinary Fellows numbered 690 and Students 47.

The changes in the membership of the Society during the year are shown in the appended table:

	Total Dec. 31, 1927	Changes during 1928	Total Dec. 31, 1928
<i>Honorary Fellows</i>	11	Elected ... .. 1 Deceased ... .. 2 <hr/> Net decrease ... .. 1	10
<i>Ordinary Fellows</i>	680	Elected ... .. 22 Student transfers ... .. 5 <hr/> 27 Deceased ... .. 11 Resigned or lapsed 6 <hr/> 17 Net increase ... .. 10	690
<i>Students</i> ...	27	Elected ... .. 25 Trans. to Fellow ... .. 5 <hr/> Net increase ... .. 20	47
<i>Total Membership</i>	718	Net increase ... .. 29	747

## REPORT OF THE HON. TREASURER

THE Income for the year 1928 exceeded the Expenditure by £98. 3s. 7d.

The Society has not received any remission of taxes on its investment income for the years 1926 and 1927. The Council of the British Association is greatly assisting the various scientific societies in connection with their claims for refund of income tax on investment dividends; and it is hoped that on a future occasion it will be possible to report that the taxes have been refunded.

The Cambridge University Press being unable to undertake the work connected with the publication of the *Proceedings* and other publications of the Society, it was decided that, with the help of the Institute of Physics, the Society would act as its own publisher. A new financial arrangement was therefore provisionally made with the Institute, dating from April 1st, 1928.

The Society desires to thank the Council of the Royal Society for a grant of £150 towards the cost of its publications. This has enabled the Society to reprint one of the numbers of its *Proceedings*, and to put in hand the publication of a special report.

A legacy of £4. 14s. 6d. (£5. 5s. 0d. less probate duty) was received in February, 1928, from the Executors of the late Mr W. H. Gray.

The sum of £100 was invested in 5 % War Loan Stock 1929/47 in June, 1928.

The investments have been valued at market prices through the courtesy of the Manager of the Charing Cross Branch of the Westminster Bank.

(Signed) ROBERT S. WHIPPLE  
*Honorary Treasurer.*

March 5th, 1929

# INCOME AND EXPENDITURE ACCOUNT FOR THE YEAR ENDED 31ST DECEMBER, 1928

1927			1927			1927		
£	s.	d.	£	s.	d.	£	s.	d.
EXPENDITURE			By			INCOME		
£	s.	d.	£	s.	d.	£	s.	d.
400 0 0	Stock of Publications at 1st January, 1928	500 0 0	500 0 0	Stock of Publications at 31st December, 1928				
475 0 0	"Science Abstracts"	535 0 0		Subscriptions:				
922 0 8	Ordinary Publications:		1113 17 1	Fellows*	1128 14 2			
73 15 4	"Proceedings"	959 8 0	9 9 0	(Voluntary)	24 19 6			
101 17 3	"Bulletin"	61 14 9	8 5 0	Students	16 13 0			
	General	93 17 2		For "Science Abstracts" and Advance Proofs	60 7 0			
188 12 7	Reprinting Parts of "Proceedings"	1114 19 11	64 5 0					
105 0 10	Postage on Publications	52 5 9	1195 16 1	Less Subscriptions written off				1280 13 8
61 8 5	Reporting at Meetings	103 2 7	4 4 0					
33 15 2	Expenses at Meetings	62 3 6						
485 15 10	Exhibition Expenses	32 3 1	1191 12 1	Sale of Publications				726 5 5
10 4 5	Optical Society Exhibition Account	576 13 5	630 16 2	Advertisements in "Proceedings"				40 3 0
		45 12 6		Dividends from Investments and Bank Interest	208 11 1			
5 0 0	Periodicals and Library	622 5 11		Less: Transferred to Duddell Memorial Fund	20 0 0			
112 10 0	Administration Expenses:	13 10 10						188 11 1
100 8 7	Institute of Physics	104 14 8		Exhibitors' Payments on account of Exhibition Catalogue				620 0 9
	Office Expenses	100 18 0		Royal Society Grant for Publications				150 0 0
20 0 0	Special Expenses on transfer of Publishing Guthrie Lecture (Honorarium)	205 12 8		Bristol Meeting: Receipts from sale of Railway Tickets				47 3 9
384 15 0	Bristol Meeting: Railway Expenses	96 6 1		Excuse Excursion: Receipts from sale of Tickets				
26 13 6	Expenses of Eclipse Excursion	20 0 0		A. W. Scott Bequest				
255 11 7	Expenses of Delegates to Volta Congress and Fresnel Centenary	47 3 9						
	A. W. Scott Bequest: Purchase of £250 5 % War Loan							
29 14 8	Balance being excess of Income over Expenditure carried to Accumulated Fund	98 3 7						
£3792 3 10		£3502 17 8	£3792 3 10					£3502 17 8

\* Seventy-seven Fellows paid reduced subscriptions by the arrangement with the Institute of Physics, the total rebate amounting to £27. 10s. 4d.

+ "Voluntary Subscriptions" are subscriptions paid by Fellows who compounded for the low sum of £10.

## BALANCE SHEET AT 31ST DECEMBER, 1928

LIABILITIES		£	s.	d.	£	s.	d.
<i>Accumulated Fund:</i>							
Balance as per last Account	.	.	.	.	1996	1	7
Entrance Fees, 1928	.	.	.	.	18	18	0
					<hr/>		
Add Increased value of Investments	.	.	.	.	2014	19	7
Excess of Income over Expenditure, 1928	.	.	.	.	18	14	0
					98	3	7
					<hr/>		
					2181	17	2
<i>Life Compositions:</i>							
As per last Balance Sheet	.	.	.	.	2289	10	0
<i>Duddell Memorial Trust Fund:</i>							
As per last Balance Sheet	.	.	.	.	480	12	9
Add Increased value of Investments	.	.	.	.	7	0	0
					<hr/>		
					487	12	9
<i>W. F. Stanley Trust Fund (For the "Bulletin"):</i>							
As per last Balance Sheet	.	.	.	.	386	0	0
Less Decreased value of Investments	.	.	.	.	25	0	0
					<hr/>		
					361	0	0
<i>A. W. Scott Bequest</i>	.	.	.	.	250	0	0
<i>Sundry Creditors</i>	.	.	.	.	536	4	11
<i>Subscriptions paid in Advance</i>	.	.	.	.	48	7	8
					<hr/>		
					£8054	12	6

<i>Investments at Market Value on date:</i>	£	s.	d.	£	s.	d.
£399 London Midland and Scottish Railway 4 % Debiture Stock . . . . .	328	0	0			
£1000 London Midland and Scottish Railway 4 % Preference Stock . . . . .	730	0	0			
£200 Metropolitan Board of Works 3½ % Stock . . . . .	198	0	0			
£400 Lancashire Corporation 3 % Redeemable Stock . . . . .	234	0	0			
£234, 2s. 9d. New South Wales 5 % Stock 1935/55 . . . . .	250	0	0			
£300 Southern Railway Preferred Ordinary Stock . . . . .	225	0	0			
£442 Southern Railway Deferred Ordinary Stock . . . . .	136	0	0			
£500 London and North Eastern Railway 4 % Debiture Stock . . . . .	390	0	0			
£500 India 3½ % Stock . . . . .	350	0	0			
£650 4 % Funding Loan 1960/90 . . . . .	555	0	0			
£650 5 % War Loan 1929/47 Inscribed "A," Account . . . . .	698	0	0			
£400 5 % War Loan 1929/47 Inscribed "B," Account . . . . .	411	0	0			
£150 Southern Railway 5 % Debiture Stock . . . . .	143	0	0			
<i>Stock of Publications (as per Treasurer's Valuation)</i> . . . . .	4703	0	0			
<i>Subscriptions due</i> . . . . .	500	0	0			
<i>Sundry Debtors</i> . . . . .	46	4	0			
<i>Cash at Bank:</i> . . . . .	40	3	0			
On Deposit Account . . . . .	27	10	10			
Current Account . . . . .	7	7	10			
<i>Cash in Hand</i> . . . . .	737	14	8			
	£9054	12	6			

ROBERT S. WHIPPLE, *Honorary Treasurer.*

We have audited the above Balance Sheet and have obtained all the information and explanations we have required. We have verified the Bank Balances and the Investments. In our opinion such Balance Sheet is properly drawn up so as to exhibit a true and correct view of the state of the Society's affairs according to the best of our information and the explanations given to us and as shown by the books of the Society.

SPENCER HOUSE, E.C. 2  
22nd February, 1929.

**KNOX, CROPPER & CO.,**  
*Chartered Accountants.*

**Examined and approved on behalf of the Society**

(Signed) L. HARTSHORN.  
(Signed) E. H. RAYNER.



# LIFE COMPOSITION FUND AT DECEMBER 31ST, 1928

	£	s.	d.
128 Fellows paid £10	.	.	1280 0 0
8 Fellows paid £15	.	.	45 0 0
1 Fellow paid £20	.	.	20 0 0
1 Fellow paid £20. 10s.	.	.	20 10 0
14 Fellows paid £21	.	.	294 0 0
20 Fellows paid £31. 10s.	.	.	630 0 0
			<u>£2289 10 0</u>

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## W. F. STANLEY TRUST FUND (FOR THE "BULLETIN").

	£	s.	d.		£	s.	d.
£300 Southern Railway Preferred Ordinary Stock	225	0	0	Carried to Balance Sheet . . . . .	861	0	0
£442 Southern Railway Deferred Ordinary Stock	136	0	0				
	<u>£361</u>	<u>0</u>	<u>0</u>		<u>£361</u>	<u>0</u>	<u>0</u>

## DUDELL MEMORIAL TRUST FUND.

CAPITAL.			
	£	s.	d.
£400 War Loan 5 % 1929/47 Inscribed Stock	411	0	0
			Carried to Balance Sheet .
	£	s.	d.
	411	0	0
REVENUE.			
	£	s.	d.
Balance at 31st December, 1927	26	12	9
Dividends	20	0	0
			Honorarium to Medallist
			Balance carried to Balance Sheet

# THE PROCEEDINGS OF THE PHYSICAL SOCIETY

VOL. 41, PART I

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## AN EXPERIMENTAL STUDY OF THE ANTICLASTIC BENDING OF RECTANGULAR BARS OF DIFFERENT CROSS-SECTIONS

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**ABSTRACT.** This paper describes a method for the survey of the surface of a beam bent by couples, with special reference to the study of the curvatures in and perpendicular to the plane of bending.

WITHIN certain limits, a uniform bar under the action of pure couples is bent into the arc of a circle, and the cross-section of the bar, originally rectangular, is now bounded by the arcs and radii of a system of concentric circles. The circumstances in which these conditions hold are determined by the condition that if the original cross-section be that of a rectangle of breadth  $2b$  and depth  $2c$ , then  $b^2$  must be small compared with  $Rc$ , where  $R$  is the radius of curvature in the plane of bending\*. In these circumstances the transverse radius of curvature will be constant, and equal to  $R/\sigma$ , where  $\sigma$  is Poisson's ratio. A large number of methods for the determination of Poisson's ratio have been based on this relation, and one object of this paper is to provide material for a critical study of such methods and for an examination of the reliability of the value of  $\sigma$  so determined.

The chief points which we propose to discuss are:

(i) Is the bar, when bent by couples applied over knife-edges in the usual manner, always bent into the arc of a circle when the amount of bending is restricted to that contemplated in the theory as usually developed? If not, what curve best represents the outline of the bar?

(ii) What is the nature of the transverse curvature in similar circumstances?

(iii) How does the transverse curvature vary with distance from an origin taken midway between the knife-edges?

(iv) How does the value of  $\Sigma$ , the ratio of the curvatures at this origin, measured for a small amount of bending, vary with variations of the ratio of the breadth to the depth of the beam? In particular, is any departure from the value of Poisson's

\* Prescott, *Applied Elasticity*, p. 40.

ratio  $\sigma$ , as determined directly by experiments made on the specimens concerned by means of extensometers, conditioned by the failure of the relation just given, that  $b^2$  must be small compared with  $Rc$ ?

(v) Is the value of  $\Sigma$  for any one bar dependent on the amount of bending? If so, what equation best represents the relation between  $\Sigma$  and  $R$ ? In particular, is it possible to find a limiting value ( $\Sigma_0$ ) of  $\Sigma$  corresponding to zero bending, which, under proper conditions, shall be in sensible agreement with  $\sigma$  as determined directly by the extensometer?

### § 1. HISTORICAL NOTES

F. Neumann, by fixing mirrors on the sides of a rectangular beam bent by couples, is said to have shown\* the nature of the change of shape of the cross-section, but his experiments were, apparently, qualitative. Mallock† inserted four long fine steel wires into holes drilled normally into the upper surface of the beam, and determined  $\Sigma$  from observation of the changes in the inclination of these wires with changes in the bending couple.

If the four wires of this experiment are replaced by short pillars and mirrors are attached to the upper ends of these pillars we have a more sensitive means of measuring the change of inclination and hence determining  $\Sigma$ . This method has been worked out by Carrington‡.

Searle§ describes a simple method for measuring the transverse curvature by soldering two vertical rods to the sides of the bar under experiment, and measuring directly the amount of approach of their upper extremities as the beam is bent. The sensitiveness of this method has been considerably increased by I. Williams||, who uses a mirror depending from a bifilar suspension attached to the upper ends of the rods. All these are open to criticism, inasmuch as the beam is tampered with by solderings or by other methods of attachment made in the immediate neighbourhood of those parts of the beam whose behaviour is under investigation. Moreover, in most of these experiments no attempt is made to correct for initial curvature, and the values of  $\Sigma$  so found are subject to considerable variations among themselves.

Optical methods have been used, and these, in so far as they involve no tampering with the bar, must be considered as superior to the methods already described. Cornu¶ first pointed out that the fringes produced in monochromatic light by the air film between the bent beam and a flat surface form a family of hyperbolas, the angle  $\alpha$  between their asymptotes being related to the ratio of the curvatures at the origin by the equation

$$\tan^2 \frac{1}{2} \alpha = \Sigma.$$

The method has been studied in considerable detail by Straubel\*\* and later by Jessop††, corrections being introduced for initial curvature of the beam. In some

\* Vide I. Williams, *Phil. Mag.* 24, 886 (1912).

† A. Mallock, *Phil. Mag.* 29, 157 (1879).

‡ H. Carrington, *Phil. Mag.* 41, 206 (1921).

§ G. F. C. Searle, *Experimental Elasticity*, p. 114.

|| *Loc. cit.*

¶ A. Cornu, *Comptes Rendus*, 69, 333 (1869).

\*\* R. Straubel, *Ann. der Physik*, 68, 369 (1899).

†† H. T. Jessop, *Phil. Mag.* 42, 555 (1921).

of the earlier experiments the distance between the knife-edges, considered in relation to the dimensions of the beam, was far too small, and Jessop has investigated the effect of the separation of the knife-edges and of the mode of support of the beam thereon. The effect of astigmatism in a beam of light reflected from the surface has been utilised by Searle\* to determine the elastic constants of glass, and Andrews† has shown that  $\Sigma$  may be determined from measurements of the diffraction haloes produced when lycopodium powder is dusted on the polished surface of a bent beam. Baker‡ uses interference methods, but solders the holder for the interferometer on to the bar. He finds that  $\Sigma$  is independent of the stress up to values of the stress of 10,000 lb./sq. inch, and that for rectangular bars of different cross-section,  $\Sigma$  is a linear function of the ratio of the breadth to the depth, decreasing as this ratio increases.

## § 2. THEORY

The theory of the anticlastic bending of a rectangular bar under the action of couples is fully discussed by Love§ and Prescott||. It is sufficient for our purposes to note that if, taking axes as shown in Fig. 1 (f), we assume a system for which the stress component  $X_x$  is equal to  $Eaz$ ¶, all the remaining stress components vanishing, we find without difficulty that the equation to the curve into which points originally on the  $x$  axis are displaced is

$$z = -\frac{1}{2}ax^2,$$

and that the bending moment over any cross-section is  $EaAk^2$ . Hence the beam is bent into a parabola, and the radius of curvature  $R$  at any point of the beam is given by

$$R^{-1} = a - \frac{3}{2}a^2x^2,$$

approximately. Thus as far as elementary theory is concerned the identification of the curve of bending with a circle is justified if  $x^2/R^2$  is negligibly small in comparison with unity. The shape of the distorted cross-section is readily worked out, and it is seen that the lines

$$z = \pm c$$

become

$$z = \pm c + \frac{1}{2}a\sigma(y^2 - c^2),$$

which is simply the parabola

$$z = \frac{1}{2}\sigma ay^2$$

displaced. Hence both longitudinal and transverse curvatures are similar in character, and  $\sigma$  is simply the ratio of the radii of curvature of these parabolas at the origin. It follows that a method such as that devised by Mallock, which measures curvatures in the neighbourhood of the origin, is, *ceteris paribus*, more

\* G. F. C. Searle, *Proc. Cam. Phil. Soc.* 21, p. 772 (1923).

† Jas. P. Andrews, *Phil. Mag.* 2, 945 (1926).

‡ Baker, *Phil. Mag.* (1924).

§ Love, *Mathematical Theory of Elasticity*.

|| Prescott, *Applied Elasticity*.

¶  $E$  stands for Young's Modulus.

likely to give results in accordance with elementary theory than those methods which depend on the assumption of a circular outline over a wide range.

The relations which we have been discussing hold for points between the knife-edges, and indeed, in terms of the general theory, they hold there only for those points for which  $x^2/R^2$  is small in comparison with unity. Outside the knife-edges we are dealing with a modified cantilever problem, and the equation to the curve into which points originally on the  $x$  axis are displaced is of the type

$$y = A - Bx + Cx^2 - Dx^3.$$

It will, however, be seen in the sequel that, empirically at least, the curve of longitudinal section of a bar bent by couples can be very closely represented by equations which are valid both inside and outside the knife-edges, holding good almost to the points of application of the load.

### §3. METHODS

(a) The longitudinal curvature of a bar bent by couples may conveniently be studied by coating the edge of a bar with white paint and photographing the painted edge. Lantern slides prepared from these photographs, and projected on to a screen of squared paper, enable the  $x, y$  co-ordinates of the curve with respect to any arbitrarily chosen co-ordinate axes to be read off at once. The lenses used were tested for any possible distortions by photographing a *réseau*, a straight-edge and an arc of a circle, and measuring the resultant photographs. The results of these tests were quite satisfactory. Some attempts were made to study the transverse curvature by laying a straight-edge across the bent bar, and photographing the gap between the straight-edge and the bent bar. The resulting negative was measured under the microscope, but the result obtained could only be considered a rough approximation.

(b) An optical method was used which had the advantage that it permitted the contouring of the whole surface of the bent beam, where that considered desirable. A very fine pencil of light, isolated from a parallel beam by means of a stop with a pinhole aperture, impinges on the bent plate at its centre of symmetry, so that it is reflected along its incident path, and is received on a screen distant about 2 metres from the bar, where it forms a small but definite patch of light. The bar is then traversed by equal steps along a line perpendicular to the normal at its centre, and the position of the reflected spot is observed. From these observations the co-ordinates of any point on the line which originally coincided with the  $x$  axis may easily be deduced.

Let  $RQP$  represent (on an exaggerated scale) the required curve, and let  $RS = QT = d$ , the amount of each horizontal traverse. With the notation shown it may be seen that  $\angle PQT = \frac{1}{2}\phi_1$  and  $\angle QRS = \frac{1}{2}(\phi_1 + \phi_2)$ , so that if  $PT = y_1$ ,  $P'R = PT + QS = y_2$ , then

$$y_1 = d \tan \frac{1}{2}\phi_1,$$

$$y_2 = d [\tan \frac{1}{2}\phi_1 + \tan \frac{1}{2}(\phi_1 + \phi_2)],$$

and in general

$$y_n = d [\tan \frac{1}{2} \phi_1 + \tan \frac{1}{2} (\phi_1 + \phi_2) + \dots + \tan \frac{1}{2} (\phi_{n-1} + \phi_n)].$$

If the deflections are such that we may replace tangents by angles,

$$y_n = d (\phi_1 + \phi_2 + \dots + \phi_{n-1} + \frac{1}{2} \phi_n).$$

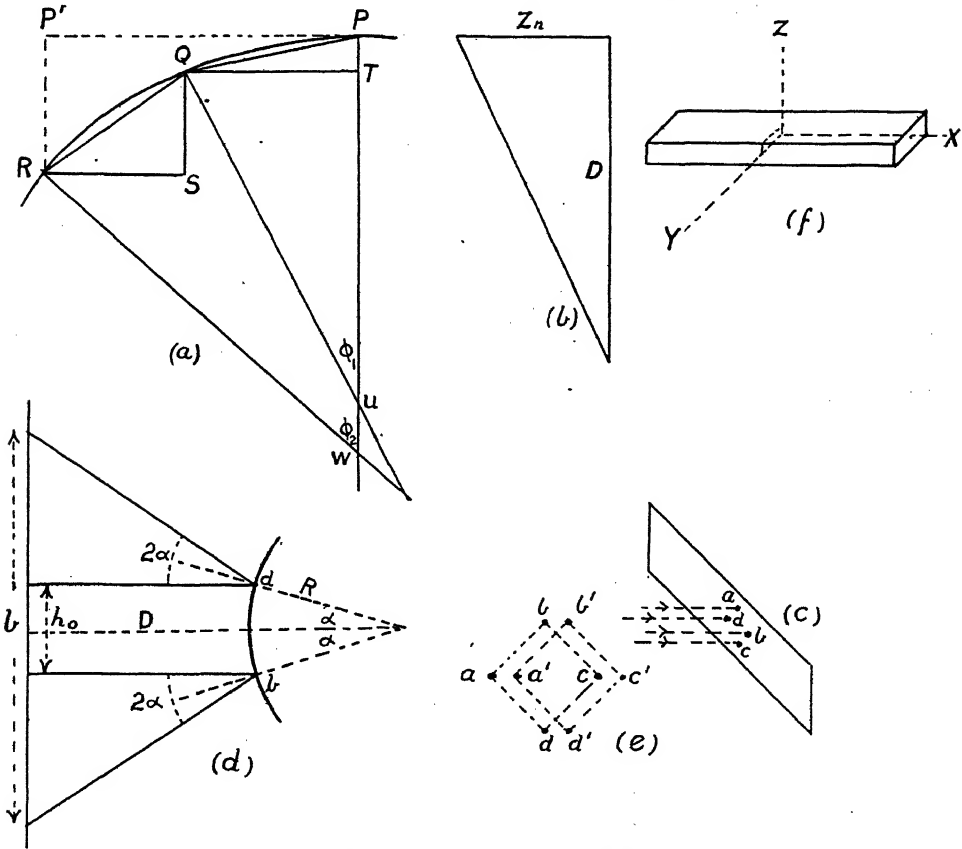


Fig. 1. Theoretical diagrams.

Suppose now that the reflected beam falls on a screen placed at a shortest distance  $D$  from the plate, Fig. 1, so that the beam reflected from  $P$  meets it normally. If then, corresponding to a traverse of  $x_n$  (equal to  $nd$ ), the reflected beam is turned through an angle  $2\phi_n$ , and the spot on the screen is deviated through a distance  $z_n$ , we have

$$\phi_n = z_n/2D,$$

and

$$y_n = \frac{d}{2D} \left( z_1 + z_2 + z_3 + \dots + z_{n-1} + \frac{z_n}{2} \right) \dots\dots(1).$$

The required curve is now obtained by plotting values of  $y_n$  against the corresponding values of  $x_n$ . In a similar manner the transverse curvature may be investigated.

The ratio  $\Sigma$  of the curvatures in the neighbourhood of the origin may or may not coincide with the value of Poisson's ratio  $\sigma$  as determined directly by

experiments with the extensometer.  $\Sigma$  is most readily determined by using pencils of light in place of the thin wires of Mallock's experiment. Four fine pencils are isolated from a parallel beam of light by means of a stop pierced with four pin-holes placed approximately at the corners of a square. These four pencils fall on the bar as shown at (c) and are reflected as before on to a screen at a distance  $D$ .

If  $h_0$  and  $v_0$  be the "horizontal" and "vertical" distances on the screen corresponding to the points ( $d$  and  $b$ ) and ( $a$  and  $c$ ) respectively, and  $h$  and  $v$  are the corresponding distances when the plate is bent, we have, Fig. 1 ( $d$ ), with the usual assumptions,

$$\frac{h - h_0}{2D} = \frac{bd}{R}; \quad \frac{v - v_0}{2D} = -\frac{ac}{R_1}.$$

Hence  $\Sigma$ , the ratio of the curvatures at the origin, is given by

$$\Sigma = -\frac{bd}{ac} \frac{v - v_0}{h - h_0} \quad \dots\dots(2).$$

If we, therefore, plot  $(v - v_0)$  against  $(h - h_0)$  we shall, if  $\Sigma$  be constant, obtain a straight line, the slope of which will be proportional to  $\Sigma$ . If  $\Sigma$  vary, it is, at any point, proportional to the ratio of ordinate to abscissa at the point in question.

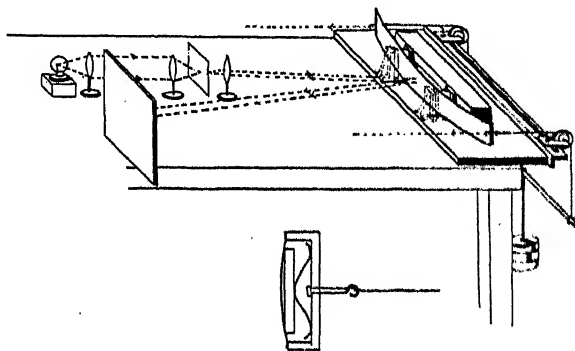


Fig. 2. Experimental arrangements.

The experimental arrangements are indicated in Fig. 2, which is almost self-explanatory. The source of light was a Pointolite, and the manner of applying a variable couple to the bar is shown in sufficient detail in the figure. By traversing the bar in the manner already explained, a series of values of  $x$  could be obtained, and from these the corresponding values of  $y$  deduced by means of equation (1). A series of readings was always taken on the unbent plate, so that a correction might be applied if necessary to the values obtained in any particular experiment.

#### § 4. RESULTS

##### (i) *The longitudinal curvature of a uniform rectangular bar bent by couples.*

A brass bar of length 60 cm., breadth 5 cm., depth 0.23 cm., was supported against two knife-edges 20 cm. apart in the manner shown in Fig. 2. Table I below shows the results of an exploration of the bar by the method of the deflected pencil.

Table I: Typical results for brass bar.

$D = 239$  cm.,  $d = 2.54$  cm.; hence  $d/2D = 0.00533$ .

Bent by couple $2 \times 10^4$ gm. cm.			Cor- rection, from unbent plate	Correct	Bent by couple $4 \times 10^4$ gm. cm.		Correct
$x_n$	$z_n$	$y_n$		$y_n$	$z_n$	$y_n$	$y_n$
cm.	cm.	cm.	cm.	cm.	cm.	cm.	cm.
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2.5	1.35	0.0036	0.0055	0.0091	4.50	0.012	0.017
5.1	3.50	0.016	0.021	0.037	9.15	0.048	0.069
7.6	6.20	0.042	0.042	0.084	14.20	0.110	0.152
10.2	9.75	0.085	0.063	0.148	20.65	0.202	0.265
12.7	10.70	0.138	0.090	0.228	23.55	0.320	0.410
15.2	13.10	0.202	0.124	0.326	28.40	0.459	0.583
17.8	21.80	0.294	0.142	0.436	39.45	0.635	0.777
20.3	26.00	0.421	0.138	0.559	45.25	0.865	1.00
22.8	25.50	0.560	0.137	0.697	45.95	1.10	1.24
25.4	24.10	0.692	0.146	0.838	45.35	1.35	1.50
27.9	24.80	0.821	0.163	0.984	44.75	1.58	1.74

These figures are typical of a large number obtained. As we have seen, elementary theory assumes a parabolic outline, which for small strains becomes indistinguishable from a circle. That is, when  $y$  is very small compared with  $x$  it is a matter of indifference whether we plot  $x^2$  or  $(x^2 + y^2)$  against  $y$  to obtain a rectilinear graph. In actual fact, a plot of  $x^2$  against  $y$  shows distinct curvature (see Fig. 3) for the portion of the beam between the knife-edges, even though the elevation of the beam at the centre is quite small. This serves to emphasise the statement that measurements of longitudinal curvature depending on applications of the formula  $R = (x^2 + y^2)/2y$  to a beam bent by couples ( $y$  being the elevation midway between knife-edges at a distance of  $2x$  apart) must be made with considerable caution, and this fact should be borne in mind in measurements of Young's modulus made by uniform bending methods.

If we plot  $y/x^2$  against  $x^2$  we obtain a curve which is very fairly rectilinear from the origin almost to the points of application of the load. There is no marked change in passing through the points at which the knife-edges are situated, and we may therefore take the equation

$$y = ax^2 - bx^4 \quad \dots\dots(3)$$

as representing with considerable accuracy the outline of the beam over almost its entire length\*. Fig. 3 shows the outline of two bars, and gives some conception

\* In some of the specimens examined the equation  $y = ax^2 - bx^4$  strictly represented the facts throughout the whole range considered; in other specimens the simple parabolic formula represented the facts over the region between the origin and the first knife-edge, with perhaps a little greater accuracy. The fourth power term represents over this region only a very small addition, and its introduction displaced the calculated points from the experimental points by amounts which were only a very little greater than the unavoidable errors of experiment; but since the displacements were in every instance in the same direction, we have deemed it advisable to record this fact.





the curvature, as far as terms in  $x^2$  are concerned, is given by

$$R^{-1} = 2a - 12a^3x^2,$$

and it is usual to take it as constant and equal to  $2a$ . If we take equation (2) as representing the outline of the bar we easily find that

$$1 + (2ax - 4bx^3)^2 = (2a - 12bx^2)^{\frac{2}{3}} R^{\frac{2}{3}}.$$

The additional terms are often quite appreciable for the values of  $x$  met with in the ordinary cases, where measurements are made on the assumption of circular curvature, and it is not uncommon to find that the curvature at the knife-edges may differ from the curvature at the origin by as much as 1 or 2 per cent.

It may be noted that the curves connecting  $x^2$  and  $y$  flatten out as the bending is increased, and that at considerable curvatures—in many instances quite outside the range suggested by the elementary theory—the longitudinal curvature becomes very closely parabolic. This condition may be very closely realised in the thinner plates which may be subjected to considerable bending without serious permanent deformation. An instance is given in Table III below.

Table III

Rolled brass bar,  $30.6 \times 2.80 \times 0.062$  cm. Couple = 1600 gm. cm.

$x$	0	10	20	30	40	50	60	70	80	90	100	110	120
$x^2 \cdot 10^{-3}$	0	1.0	0.4	0.9	1.6	2.5	3.6	4.9	6.4	8.1	10.0	12.1	14.4
$y$ , cor.	0	0.2	0.8	1.8	3.4	5.2	7.8	10.8	14.1	18.1	22.3	27.1	31.7
$x^2/y$	—	0.50	0.50	0.50	0.47	0.48	0.46	0.46	0.46	0.45	0.45	0.44	0.45

Similar investigations were carried out by the alternative photographic method described, with results which confirm those arrived at by the deflected beam method. An example of the results obtained is shown in Table IV below.

Table IV

Rolled brass bar,  $30.3 \times 2.78 \times 0.137$  cm. Formula,  $y = ax^2 - bx^4$ .

$x_n$	Couple 8000 gm. cm.		Couple 17,000 gm. cm.	
	$a = 0.000352,$ $b = 2.21 \times 10^{-9}$		$a = 0.000665,$ $b = 5.00 \times 10^{-9}$	
	$y_n$ observed	$y_n$ calculated	$y_n$ observed	$y_n$ calculated
cm.	cm.	cm.	cm.	cm.
0.0	0.0	0.0	0.0	0.0
1.17	0.0	0.03	0.1	0.07
2.34	0.1	0.14	0.2	0.26
3.51	0.2	0.31	0.4	0.70
4.68	0.4	0.56	0.8	1.05
5.85	0.8	0.87	1.4	1.64
7.02	1.2	1.24	2.15	2.32
8.19	1.7	1.67	3.1	3.14
9.36	2.2	2.17	4.0	4.06
10.53	2.9	2.70	5.1	5.05
11.70	3.4	3.30	6.2	6.15
12.87	4.1	3.94	7.3	7.30
14.04	4.7	4.61	8.5	8.54
15.15	5.0	5.33	9.9	9.78

- (ii) *The transverse curvature of a uniform rectangular beam bent by couples, and*  
 (iii) *The variation of transverse curvature with distance along the beam.*

This curvature was investigated by the reflected beam method, with the difference that it was found more convenient in traversing any given section to move the perforated diaphragm rather than to move the bar. The curvature was investigated at the origin and at different points along the bar. Table V shows a typical series of figures.

Table V

Dimensions of bar,  $60 \times 5 \times 0.23$  cm.

Transverse distance from centre $y_n$	Mean deflection $z_n$		$z_n$ correct	Mean deflection $z_n$		correct
	Bent	Unbent		Bent	Unbent	
cm.	cm.	cm.	cm.	cm.	cm.	cm.
0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.5	0.18	1.52	1.02	1.30	1.62	0.32
1.0	1.12	3.14	2.02	2.48	3.27	0.79
1.5	1.95	4.92	2.97	3.90	4.87	0.97
2.0	3.90	6.95	3.05	5.60	7.15	1.55
	$x = 0$			$x = 18$ cm.		

If we assume that the transverse curvature is constant and equal to  $R_1^{-1}$ , we may test this constancy rapidly as follows. We have, with symbols analogous to those in Fig. 1,

$$2\phi_n = z_n/D = 2y_n/R_1,$$

$$R_1 = 2D \cdot \frac{y_n}{z_n} = 400y_n/z_n,$$

since  $D$  was equal to 2 metres.

Hence, if we plot  $y_n$  against  $z_n$ , a straight line will be obtained if the curvature is uniform, and this curvature will be numerically equal to  $1/400$  of the slope of the line. In every instance examined the lines so drawn were rectilinear within the limits of experimental error, so that the transverse curvature may be assumed uniform at all points along the bar. An investigation of the variation of transverse curvature with distance along the bar yielded the results shown in Table VI.

A plot of  $R$  against  $x^2$  was strictly linear over a wide range, both inside and outside the knife-edges. In the instance given in Table VI the results were very closely represented by

$$R_1^{-1} = 4.12 \times 10^{-3} - 6.4 \times 10^{-6}x^2 \quad \dots\dots(4),$$

as is shown by the third column in Table VI, and the curve of Fig. 4. It will be noticed that there is no marked alteration in the curve after its passage through the position occupied by the knife-edge, but that equation (4) represents the experimental facts up to a point near the point of application of the load. It is evident that, if this equation holds, there will be a point for which the transverse

curvature vanishes, and as a matter of fact such a point does exist, although, as Fig. 4 shows, its position is not given by equation (4). The point was further investigated by observation of the interference fringes formed as in experiments made by Cornu's method. Photographs were taken of the fringes on a bent glass bar, and these photographs show quite clearly that the curvature vanishes, and indeed changes sign at a point close to the end of the bar (see Plate I).

Table VI

Distance from centre	Transverse curve	
	Observed	Calculated
cm.	cm.	cm.
0	$43.8 \times 10^{-4}$	$41.2 \times 10^{-4}$
3	38.8	40.6
6	34.8	38.9
9	35.2	36.2
12	32.2	32.0
15	26.2	26.8
18	18.2	20.5
21	11.2	13.0
24	7.0	4.4
27	5.3	-5.4

(iv) *Variation of the ratio of the principal curvatures at different points along a rectangular bar bent by a constant couple.*

It follows that, if the longitudinal curvature of a beam bent by a definite fixed couple is given by

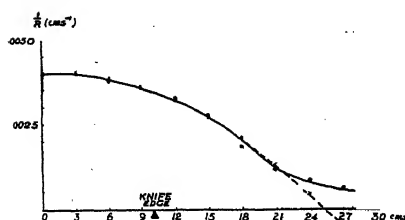
$$R^{-1} = A - Bx^2 + Cx^4,$$

and the transverse curvature is given by

$$R_1^{-1} = A_1 - B_1x^2,$$

then  $\Sigma$ , the ratio of these curvatures at any given point, will in general vary as we move along the bar, and will be given by

$$\begin{aligned}\Sigma &= R_1^{-1}/R^{-1} \\ &= (A_1 - B_1x^2)(A - Bx^2 + Cx^4)^{-1}.\end{aligned}$$



o = Observations.

x = Points on curve, equation (4).

Fig. 4. Variation of transverse curvature with distance from centre.

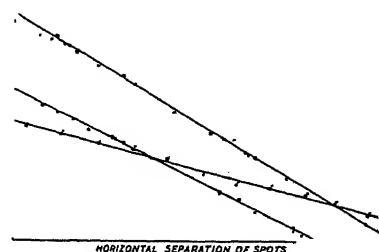


Fig. 5. Observations made by four-spot method.

(v) *The determination of  $\Sigma$ , the ratio of the principal curvatures at the origin; its variation with variation in the thickness of a rectangular bar of constant breadth; and its relations to  $\sigma$ , the value of Poisson's ratio, as determined by extensometer experiments.*

The method employed for the determination of  $\Sigma$  was the four-spot method described previously, see Fig. 1 (c) and (d). The apparatus used was that sketched in Fig. 2, with the substitution of a four-orifice for a single-orifice stop.  $\Sigma$  was calculated from equation (2), and the amount of bending was small. In this series of experiments, as indeed in all the experiments described in this paper, the knife-edges were always separated by more than three times the width of the bar.

In any one series of experiments on one bar, readings were taken with the bar bent alternately convex and concave, the bending was then increased, and the observation repeated. A curve was plotted between  $v$  and  $h$ , and the value of  $\Sigma$  was deduced from the slope of the curve. With the amount of bending employed these curves were always rectilinear (see Fig. 5).

For each bar this series of operations was repeated from four to six times, and a mean value of  $\Sigma$  taken.

The bar under experiment was then tested in an Avery 10-ton testing machine, which was placed at our disposal by the kindness of Professor E. H. Lamb. Longitudinal extensions and the corresponding lateral contractions were both read by instruments of Professor Lamb's\* design. Fig. 6 (Plate I) shows a bar under test, with the extensometers *in situ*. Plots of the deflections of the two extensometers for different bars are exhibited in Fig. 7, and it will be seen that they are strictly rectilinear, so that Poisson's ratio can be deduced at once from the slopes of these curves.

It was not possible to test all the bars in this way, as some of the thinnest buckled under the pressure of the lateral extensometer.

Experiments were made with two specimens of brass. From the first specimen a number of strips of length about 30 cm. were cut. These strips were each about 2.9 cm. wide and originally 0.32 cm. thick. They were cut down to different thicknesses in the workshop of the East London College. Each specimen was polished on one side by means of a succession of graded emeries, and finished to uniform overall thickness. Table VII following shows the values of  $\Sigma$ , the ratio of the curvatures at the origin for a series of bars about 30 cm. long, 2.9 cm. wide, and of a thickness varying from about one-third of a centimetre down to one-third of a millimetre. They are compared with the values of Poisson's ratio  $\sigma$  as determined directly by means of the testing machine.

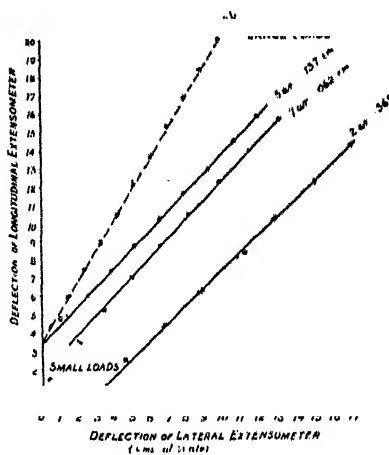


Fig. 7. Examples of testing machine results. (Slopes are inversely proportional to Poisson's ratio.)

\* E. H. Lamb, *Engineering*, Feb. 13, 1925.

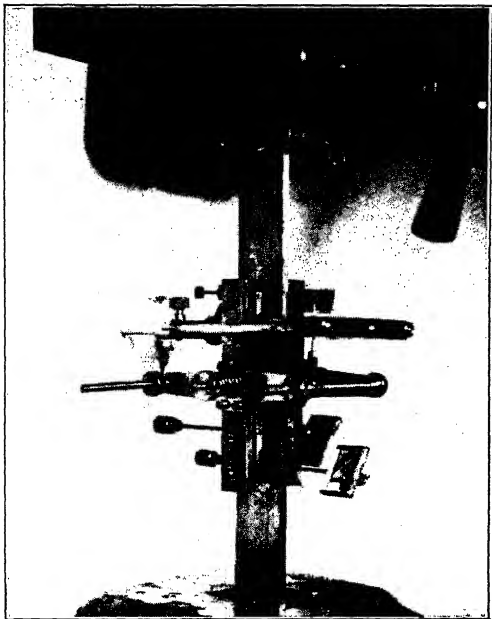


Fig. 6. Extensometers used in testing-machine



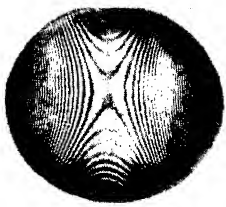
26 cms



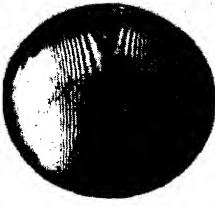
21 cms



16 cms



13 cms



8 cms



3 cms

Interference fringes on bent glass plate

(Length of plate, 60 cm. Knife-edges 20 cm. apart. Distances from end are given.)



The plates from the second specimen, instead of being cut down to different thicknesses, were rolled by Messrs Johnson & Matthey. They were annealed, and finally polished and finished to even thickness overall at the East London College. Table VIII shows the results of tests made on these specimens.

Table VII.

Thick- ness	$\Sigma$	Mean $\Sigma$	$\sigma$
cm.			
0.315	0.32 0.31 0.33 0.31 {0.32} {0.30}	0.315	0.323
0.221	0.30 0.26 0.23 0.24 0.28		
0.144	0.28 0.28 0.27 0.26		
0.114	0.25 0.26 {0.23} {0.26}	0.273	0.290
0.084	0.23 0.35 0.32 0.36 0.36 0.36	0.246	0.292
0.062	0.36 0.49 0.57 0.52	0.351	0.423*
0.038	0.56 0.76 0.66 0.63† 0.70	0.53	0.342
		0.69	

\* Verified subsequently.

† Too thin for testing machine.

Table VIII.

Thick- ness	$\Sigma$	Mean $\Sigma$	$\sigma$
cm.			
0.466	0.36 0.33 0.32 0.36	0.343	0.323
0.369	0.30 0.33 0.32 0.31		
0.262	0.32 0.32 0.32 0.32		
0.173	0.32 0.30 0.31 0.30	0.315	0.354
0.137	0.30 0.28 0.33 0.29 0.29	0.320	0.354
0.084	0.33 0.33 0.32 0.33 0.36	0.303	0.321
0.062	0.39 0.37 0.37 0.38 0.61 0.63 0.61	0.30	0.336
0.038	0.57	0.335	0.355
0.026†		0.378	0.323
		0.60 (0.76)†	0.32

† Too thin. Value given is rough approximation only.

Two possible sources of error were investigated. The plates were not polished to an optical surface, and it is probable that the variations in  $\Sigma$  shown in a set of experiments on any one plate may be due in some measure to accidental irregularities in the surface. This was tested by an experiment in which a stop with eight orifices was used in order to give two different sets of readings from which to compute  $\Sigma$ . The eight orifices were so arranged as to form two squares contiguous each to the other (cf. Fig. 1 (e)). In Table VII above, bracketed values of



$\Sigma$  indicate numbers which were obtained in this way. It may be mentioned, as confirming this view, that values of  $\Sigma$  obtained from experiments on a glass bar with a good optical surface show less variation *inter se*. The effect of additional annealing was also investigated, and Table IX below shows the effect on the value of  $\Sigma$  produced by re-annealing certain plates.

Table IX

Plate ... ..	7 ar.	8 ar.	9 ar.
Thickness, cm. ... ..	0.062	0.038	0.026
$\Sigma$ after first annealing ... ..	0.378	0.60	0.76
$\Sigma$ after re-annealing and re-polishing	0.384	0.448	0.82

It will be seen that though there is a definite effect due to additional annealing there is no alteration in the trend of the variation of  $\Sigma$  with thickness. The general result of the two sets of experiments is exhibited in Fig. 8. It is evident that in both sets of experiments Poisson's ratio  $\sigma$  as directly measured is not subject to

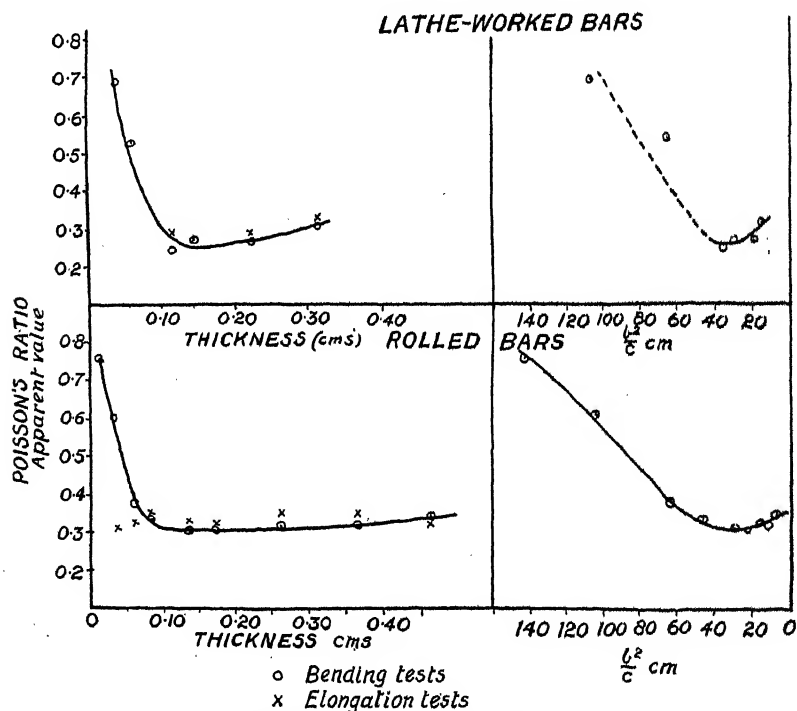


Fig. 8. Poisson's ratio for rolled and lathe-worked bars.

large variations over the range of thickness considered. The quantity  $\Sigma$ , defined as the ratio at the origin of the longitudinal to the transverse radius of curvature, decreases slightly with decreasing thickness and then rapidly increases. The variation with  $b^2/c$  is shown in the same figure, and as an average value of the radius  $R$

of longitudinal curvature employed in these experiments was about 290 cm., it will be seen that the rapid increase of  $\Sigma$  begins at values of  $b^2/Rc$  of the order 0.14.

Table X: Constants in formula  $y = axe^{-bx}$ .

Plate	Thickness	$a$	$b$	Remarks
7 ar.	cm. 0.062	0.489	0.00828	} Rolled strips Strip cut at E.L.C.
8 ar.	0.038	0.891	0.0152	
8 b.	0.084	0.339	0.00643	

Finally, we proceed to consider how the value of  $\Sigma$  for any one bar varies with the longitudinal curvature  $R$ . The experiments were carried out in the manner described in discussing the series immediately preceding, the longitudinal curvature being, however, pushed to values far exceeding those contemplated in the quantitative development of elastic theory. If  $h - h_0$  be denoted by  $x$ , and  $v - v_0$  by  $y$ , so that, as previously explained,  $\Sigma$  is proportional to  $y/x$ , it is found that, over the range of experiment, a plot of  $\log(y/x)$  against  $x$  yielded a straight line. Hence, the experimental results are expressed by the equation

$$y = axe^{-bx},$$

values of  $a$  and  $b$  for some of the plates tested are shown in Table X above, and the agreement between calculated and observed values of  $x$  and  $y$  is shown in Fig. 9.

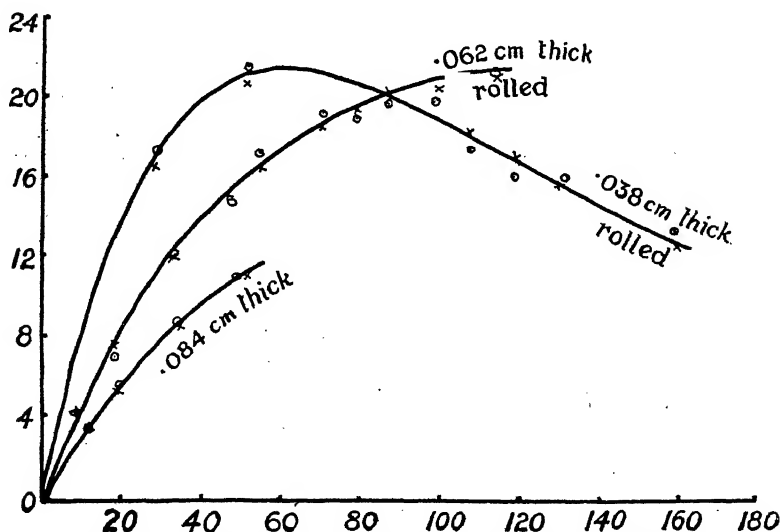


Fig. 9. Comparison of calculated (x) and observed results (o). Formula:  $y = axe^{-bx}$ .

Since  $y/x$  is proportional to  $\Sigma$ , and  $x$  is proportional to the longitudinal curvature  $R^{-1}$ , it follows that we may put

$$\Sigma = \Sigma_0 e^{-k/R}.$$

Table XI below gives values of  $\Sigma_0$  and  $k$ , calculated from this formula for certain of the plates previously tested. The values of  $\Sigma_0$  should be compared with the

values of  $\Sigma$  obtained for small finite bendings and exhibited in Tables VII and VIII. The formula, which does not profess to do more than express the result of experiments made over a definite range of curvatures, shows no indication of a possible change of sign in  $\Sigma$ .

Table XI: Constants in formula  $\Sigma = \Sigma_0 e^{-k/R}$ .

Plate	Thickness	$\Sigma_0$	$k$	Remarks
7 ar.	cm. 0.062	0.476	2.73	} Rolled strips Strip cut at E.L.C.
8 ar.	0.038	0.891	5.01	
8 b.	0.084	0.339	1.86	

To sum up: We are now in a position to answer some of the questions propounded at the outset.

(i) The shape of the bar, from origin almost to the point of application of the load, is accurately represented by the equation

$$y = ax^2 - bx^4,$$

and the corresponding longitudinal curvature by the relation

$$1 + (2ax - 4bx^3)^2 = (2a - 12bx^2)^{\frac{2}{3}} R^{\frac{2}{3}}.$$

(ii) The transverse curvature is, within the limits of experimental error, constant.

(iii) The transverse curvature at different points along the bar is given by

$$R_1^{-1} = A_1 - B_1 x^2.$$

(iv) The value of  $\Sigma$ , the ratio of the curvatures at the origin, decreases slightly with increase in the ratio  $b^2/c$ , and then increases rapidly. If  $\Sigma$  is to be identified with Poisson's ratio  $\sigma$ , such identification must be confined to the region where  $b^2/Rc < 0.14$ . In this region, comparison with extensometer values justifies the identification of  $\Sigma$  with  $\sigma$ .

(v) For any one bar, the value of  $\Sigma$  over a considerable range of bending is connected with the longitudinal curvature by the equation

$$\Sigma = \Sigma_0 e^{-k/R}.$$

(vi) Under the heading (iv) we have pointed out that within certain limits, experimentally determined,  $\Sigma$  may be taken as a measure of Poisson's ratio. Of the various methods proposed for the measurement of  $\Sigma$ , those are to be avoided which involve soldered attachments to the bar under test. Optical methods are, therefore, to be preferred, and of these methods, the authors find the deflected beam method employed in the present research simple and reliable in practice, and of the order of sensitiveness of ordinary interference methods.

Our thanks are due, and are tendered, to Professor C. H. Lees and to Professor E. H. Lamb for the facilities which they have placed at our disposal.

## DISCUSSION

Mr T. SMITH: I would suggest that a hyperbolic or somewhat similar form for the bent bar might be anticipated from very general considerations when the positions of the knife edges, the points of application of the forces, and the dimensions of the bar can be left out of account. The form found would then be that for a bar of length great compared with the distances between the points mentioned; at considerable distances from these points it would be natural to suppose the bar distorted but little from its original shape. The formula found by the authors for the central longitudinal section  $x = ay^2 - by^4$  is not inconsistent with the hyperbolic equation  $\left(\frac{n + \alpha}{\alpha}\right)^2 - \frac{y^2}{\beta^2} = 1$  for small values of  $x$ . The curvature of the transverse section would be a maximum at the centre and diminish to zero at a large distance. It would be interesting to know whether the authors' observations are consistent with the bar's assuming the form of a slice of a hyperboloid of revolution, with the axis of rotation parallel to the axis of the unbent bar. If this form were correct the ratio of the axes of the central section would be equal to Poisson's ratio, and the form of the bent bar would be completely specified by a single variable.

Mr A. G. WARREN: It seems possible that the reduction of the transverse curvature at the knife edges may be due to the fact that the knife-edge reaction tends to keep the bar flat. The differences in the mean values found for Poisson's ratio and for the ratio of the curvatures at the origin might perhaps be due to lack of homogeneity in the material, in consequence of which different methods of experiment would give different results.

Mr ANDREWS (in reply to Mr Smith): A very large number of expressions have been tried, and those given in the paper best represent the shape of the bent surface. While we have not gone into the matter from Mr Smith's point of view, we do not anticipate that the surface could be represented as he suggests.

I am in agreement with Mr Warren as to the cause of the reduction of curvature, but that explanation of the results was purposely omitted for the sake of brevity. It is very improbable that lack of homogeneity is at the root of the variation of the results for bars of different thickness; all rolled plates were annealed twice or three times, yet they gave the same type of variation as the lathe-worked bars, which were either unannealed or annealed once. Moreover, it is unlikely that lathe-working would have produced the same kind of heterogeneity as rolling.

# AN INSTRUMENT FOR THE PRODUCTION OF KNOWN SMALL HIGH FREQUENCY ALTERNATING ELECTROMOTIVE FORCES

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**ABSTRACT.** A portable instrument for the production of known electromotive force variable in frequency from 10 to 50 kilocycles and in magnitude from 0.0076 to 15,000 microvolts, is described. The instrument is intended for the calibration of amplifiers at the measurement of the strength of wireless signals of long wave-length.

THERE are many electrical measurements which necessitate the production of a small electromotive force of radio frequency and known magnitude. For example, a wireless wave produces in a receiving aerial high frequency electromotive forces which are too small for direct measurement, and high and low frequency amplification, with rectification, must usually be employed before deflection can be obtained on a measuring instrument. If a small electromotive force of known variable frequency and magnitude is injected into the receiving aerial, equal deflections of a measuring instrument will be produced, when the electromotive force induced in the aerial by the wireless wave is equal in frequency and magnitude to the locally produced electromotive force. In order to use the method of measuring the strength of wireless signals, electromotive forces of radio frequency whose magnitudes are known accurately must be produced. Portable apparatus for this purpose has been described by several writers<sup>(1)</sup> and a summary of published work to September, 1926, is available<sup>(2)</sup>.

The portable instrument shown in Fig. 1 and Fig. 5, Plate I, is designed to cover the frequency range 10 to 50 kilocycles and the intensity range 0.0076 to 15,000 microvolts. Alternating current, variable in frequency over the desired range, is generated by a valve oscillator enclosed in metal screens which prevent the formation of electric and magnetic fields external to the screens. A coil coupled inductively to the valve oscillator and connected in series with an A.C. milliammeter supplies a known alternating current to the input of an artificial line composed of series and shunt resistance elements, described in detail later. Each shunt element of this line carries  $1/\sqrt{2}$  times the current carried by the preceding element, so that the magnitude of the electromotive force available at the signalling key at the left of the diagram depends upon the section of the artificial line to which a rotating switch makes connection. By depressing this signalling key, the desired electromotive force may be injected into the amplifier circuit at a suitable place.

## § 1. THE SCREENED VALVE OSCILLATOR

The circuit used with the instrument consists of a coil tuned by a condenser and a six-valve high and low frequency amplifier with heterodyne, as shown in Fig. 1. It is necessary to screen the valve oscillator until the stray electric and magnetic fields from it are too feeble to induce a detectable electromotive force in this receiving circuit at a distance of 6 ft. As the circuit is sensitive to an electromotive force of 0.01 microvolt induced in the coil, adequate screening of the valve

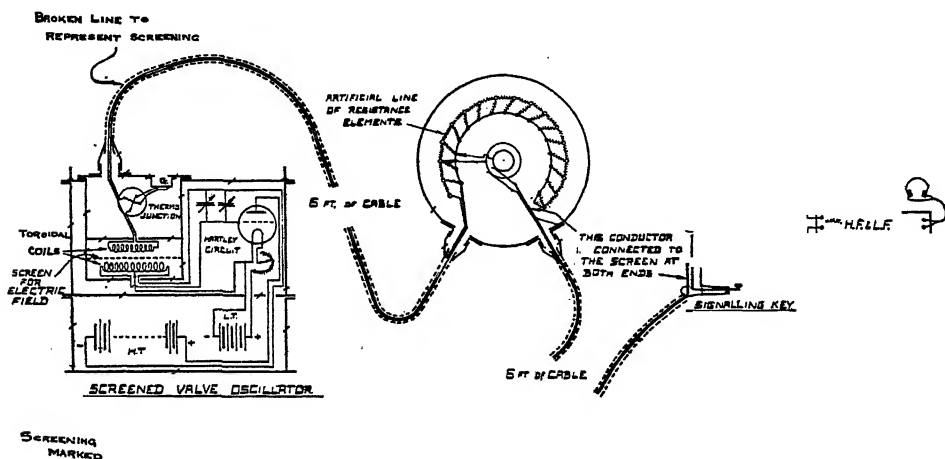


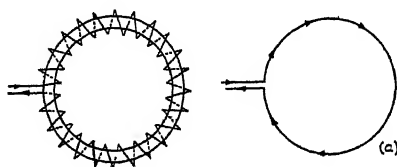
Fig. 1. Signal strength meter: screening and simplified connections.

oscillator is difficult. In the final form of instrument the magnetic and electric fields in the neighbourhood of the valve oscillator are reduced to a safe limit in three ways. The valve oscillator generates just sufficient high frequency electrical energy to produce a suitable deflection of the thermal milliammeter in the secondary circuit. The coil in the oscillatory circuit of the valve oscillator is wound in toroidal form to reduce its external magnetic field, while the external electric and magnetic fields remaining after taking these precautions are confined by enclosing the valve oscillator in metal screens.

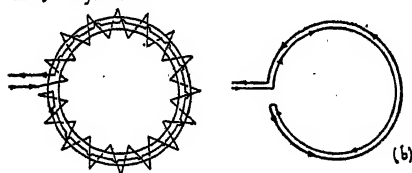
A dull emitter valve with a 66-volt high tension battery and three dry cells for filament heating generates sufficient high frequency electrical energy. Continuous frequency variation from 10 to 50 kilocycles is obtained with a number of fixed condensers controlled by a rotary switch, a variable condenser and a toroidal coil of 50 millihenries inductance. The circuit oscillates freely and supplies practically constant high frequency current to the secondary circuit over the whole range of frequency. The current in the secondary circuit is adjusted to the desired values by altering the valve filament current with a rheostat. The fixed coil of the oscillatory circuit is wound on a dust core,  $3\frac{3}{8}$  in. internal diameter,  $5\frac{3}{8}$  in. external diameter and 1 in. thick with 800 turns of No. 36 s.w.g. double-silk-covered copper

wire in a single layer. A coil of this type, wound as shown on Fig. 2 (a), produces a much weaker external magnetic field than a coil of similar size and inductance wound with circular turns in the usual way. In spite of this a quantity of energy sufficient to induce a detectable electromotive force in the receiving circuit penetrated the screens. By a slight modification in the winding, shown in Fig. 2 (b), the external magnetic field was almost eliminated and the little that remained was reduced by the screens to such an extent as to be negligible.

A Toroidal coil which produces approximately the same external magnetic field as a coil of a single turn carrying the same current



A Toroidal coil which produces very little external magnetic field.



Toroidally wound transformer for radio frequency currents, with a secondary winding screened from the electric field from the primary winding and with a screen enclosing the transformer

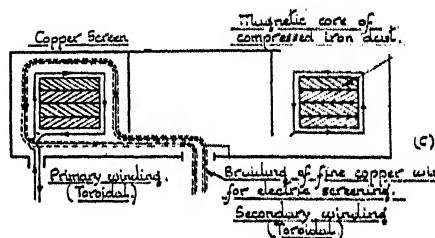


Fig. 2. Screened transformer.

Two secondary windings of 4 and 12 turns respectively are wound spirally and symmetrically round the toroid so as to reduce their external magnetic field as much as possible. The secondary windings are screened from the electric field of the primary winding by a braiding of fine copper wires, as shown in Fig. 2 (c), the braiding being connected to the metal screen round the coils. Either of these secondary windings may be connected through a vacuum thermo junction of suitable range to the artificial line by a rotating switch. The wires in this part of the circuit are twisted together in pairs to reduce stray magnetic fields.

Stray magnetic fields from the valve oscillator were more difficult to eliminate than stray electric fields. The coil which produces practically all the stray magnetic field is placed in a soldered copper box, less efficient screening being inadequate (see Fig. 3 and Fig. 7, Plate I). The vacuum thermo junctions and the switch controlling them are sufficiently screened by a copper box with a copper lid fastened with screws. The screening of the remainder of the circuit which produced most of the stray electric field was comparatively simple, two boxes and a lid cast in a light alloy of nickel chromium and aluminium being satisfactory. The dry batteries are placed in a separate compartment, so that any corrosive liquid leaking from a defective cell can do little harm.

Dials and switches external to the screens, marked *A*, *B*, *C* and *D* in Fig. 3, are provided for controlling the thermo-junction switch, the fixed air condensers, the variable air condenser and the filament rheostat respectively. These dials can be handled without producing any detectable stray fields. The control of the variable air condenser is effected by a metal rod, rotating in a metal bush in the screen and making electrical contact therewith. This rod carries, outside the screen, an ebonite handle, and inside the screen is attached to the shaft carrying the moving vanes of

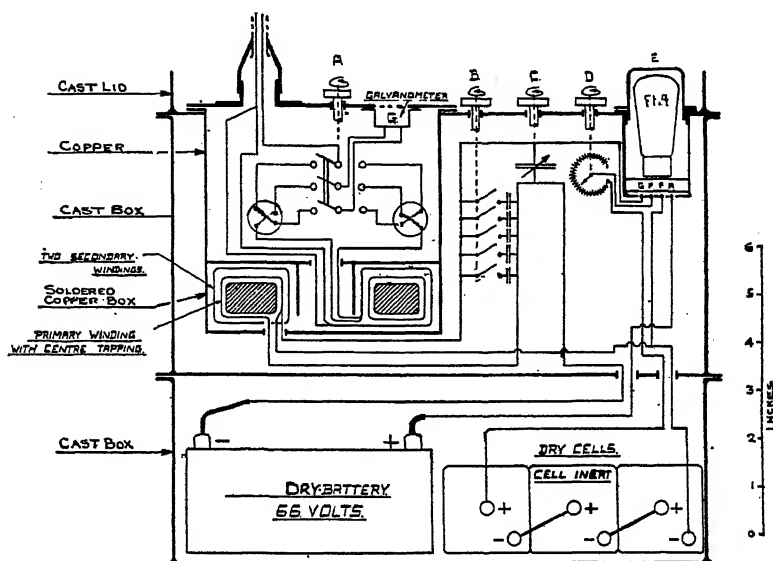


Fig. 3. Screened valve oscillator.

the condenser by a coupling of insulating material. The remainder of the condenser is fixed to the inside of the screen, but insulated from it so that the condenser is completely insulated from the screen. The change in the resistance of the screen produced by a metal rod passing through it and making good electrical contact is insufficient to cause a detectable change in the efficiency of the screening. The other external controls are similarly designed.

## § 2. THE ARTIFICIAL LINE

The artificial line consists of a network of resistances in 35 sections, each section comprising a series element of resistance  $r$  and a shunt element of conductivity  $g$ , as shown in Fig. 4. Alternating current from the valve oscillator enters the line at 1 and is divided at 2, a small part of it returning to the valve oscillator through a shunt element and the remainder passing to 3. The process is repeated at each section of the line so that each shunt element carries less current than the preceding element in a constant ratio. A calculation from the usual equations for a resistance network shows that, with a series resistance of 0.0347 ohm and a shunt conductance  $g$  of 3.47 ohms, this ratio is  $1/\sqrt{2}$ . The voltage across each shunt element is also  $1/\sqrt{2}$



times that across the preceding element, so that a rotation of the switch making contact with the ends of a shunt element by one stud in a clockwise direction reduces the potential difference between the leads to the key in the ratio  $1/\sqrt{2}$ . The input resistance of the line is 0.12 ohm, so that the electromotive force available at the signalling key is 1000 microvolts when the alternating current entering the line is 8.33 milliamperes and the rotating switch makes contact at 1. The electromotive forces available with the switch making contact at other sections of the line form the geometrical series 1000, 707, 500, 353, . . . 0.0076, the common ratio of which is  $1/\sqrt{2}$ . By supplying a current of 125 milliamperes to the line,

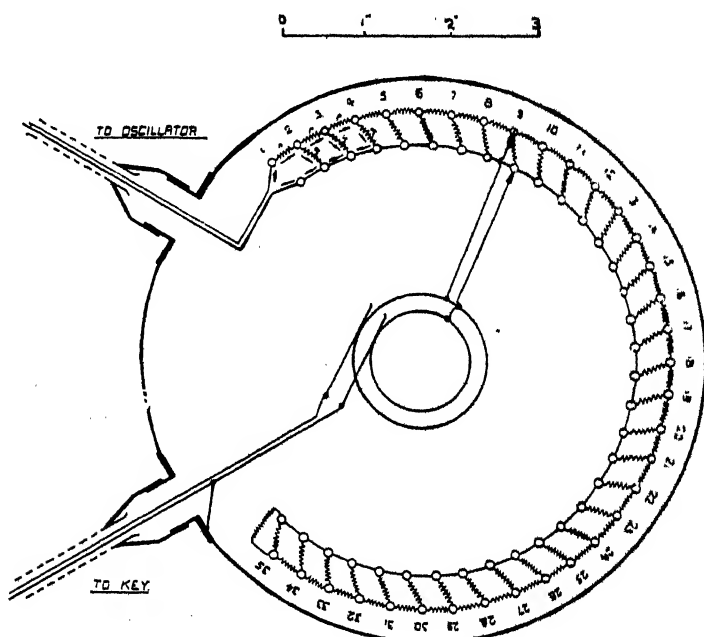


Fig. 4. Artificial line.

another geometrical series of electromotive forces ranging from 15,000 to 0.114 microvolts can be obtained. The current entering the line is measured with a suitable milliammeter connected in circuit with the switch *A* in Fig. 3.

The accuracy of the line at the highest frequency of 50 kilocycles per second depends upon the self-inductances of the elements and the mutual inductances between them. An inductance of 0.011 microhenry has a reactance of 0.00347 ohm at this frequency, which is 10 per cent. of the resistance of a series element. By arranging the connections so that loops of wire are avoided, the inductances of the elements of the line can be reduced to less than this amount. The attenuation factor of a line composed of resistance elements with comparatively small inductances in series with them can be calculated from the standard equations involving hyperbolic functions for artificial lines. It appears that the effect of the small inductances is mainly to introduce a progressive change of phase along the line. The change in the

ratio of the magnitude of the currents in successive elements is only a second order effect and is negligible provided that the reactance of an element is less than 10 per cent. of its resistance. Fortunately the change of phase along the line is of no importance in the present application.

These conclusions are confirmed by the following measurements of the ratio of the voltage across one shunt element to that across the preceding element, using direct current and alternating current at high frequencies.

Table: Ratios of voltages in adjacent shunt elements.

Sections	Direct current	Alternating current (kilocycles per sec.)			
		10·1	45·1	185	500
1-2	0·711	0·712	0·711	0·703	0·670
2-3	0·718	0·710	0·716	0·708	0·679
3-4	0·709	0·711	0·708	0·701	0·674
4-5	0·707	0·707	0·708	0·703	0·671
5-6	0·707	0·711	0·703	0·706	0·681
Mean	0·710	0·710	0·709	0·704	0·675

The attenuation factor is practically independent of frequency up to 185 kilocycles. Above this frequency a calibration must be made, a method described by D. W. Dye<sup>(3)</sup> being very convenient. By redesigning the artificial line to reduce still more the self and mutual inductances, its calibration may be made independent of frequency, at least up to 500 kilocycles. A further extension of the frequency range can be achieved by increasing the resistance of the series and shunt elements in the same proportion, thereby reducing the importance of the residual self and mutual inductances. For use at much higher frequencies, an artificial line in which both series and shunt elements are inductances would be better. The calibration of such a line should be independent of frequency over a very wide range, the lower limit being determined by the resistances of the elements and the upper limit by the capacities between them.

The wiring of the artificial line is shown in Fig. 6, Plate I, in which the series elements (No. 22 s.w.g. Eureka wire) can be seen connected to the outer row of studs. The shunt elements (No. 28 s.w.g. Eureka wire) bridge across the two rows of studs. The terminal resistance of 0·12 ohm which makes the line of 35 sections equivalent to an infinite line can be seen to the left.

### § 3. THE SIGNALLING KEY

It was found that any method of injecting an electromotive force into the resonant circuit, shown in Fig. 1, involving an abrupt change in the constants of the circuit, such as a momentary increase in its resistance, produced a noise in the head telephones. A signalling key was designed which produced no electrical disturbance in the amplifier and its circuits and no noise in the telephones. In the resting position of the key, shown in Fig. 1, the middle contact presses against the upper contact, the artificial line being disconnected. A partial depression of the

key brings the middle contact into connection with the bottom contact, connection with the top contact being maintained. Complete depression of the key disconnects the top contact, the electromotive force from the artificial line being then in series with the circuit. A resistance of about 0.1 ohm which is added to the circuit at the same time is usually too small to produce an appreciable effect.

#### § 4. THE RESIDUAL ELECTRIC AND MAGNETIC FIELDS EXTERNAL TO THE SCREENS

The continuous metal screen, completely enclosing the valve oscillator, the artificial line and the signalling key, is by no means a sufficiently perfect conductor for complete screening. A large number of joints, most of them only held together by screws, introduce resistances. The currents induced in the imperfect screen by the magnetic and electric fields generated inside it thus differ somewhat in distribution, magnitude and phase from those induced in a perfectly conducting screen. These induced currents, opposed by the resistance of the screen, give rise to potential differences over its outer surface. There are, therefore, residual electric and magnetic fields outside the screen. However, the electromotive force induced by the residual magnetic vector field from the screened valve oscillator in a coil of 10 millihenries inductance and 18 in. in diameter at a distance of 6 ft. is less than 0.01 microvolt—a quantity which can be neglected. The residual electric vector field was further reduced by connecting a point on the screen to earth. It is not possible completely to eliminate it by an earth connection because the screen is not an equipotential surface. The distribution in space of the residual electric field depends upon the point on the screen to which an earth connection is made, the point chosen being that which results in the smallest electric field in the neighbourhood of the tuned circuit and amplifier. With the connections between screen, circuit and earth, shown in Fig. 1, the residual electric field is too small to be detected, that is to say, the electromotive force induced by it in the tuned circuit connected to the amplifier is less than 0.01 microvolt. An accidental earth connection to another part of the screen alters the potential distribution over the outside of the screen and the resulting external electric field sufficiently to produce a detectable electromotive force in the tuned circuit. The effect of the high resistance connection to earth, introduced by touching any part of the screen, is not detectable.

#### § 5. USE FOR THE CALIBRATION OF VALVE AMPLIFIERS

In order to form an estimate of the quality of a valve amplifier, it is desirable to know the smallest electromotive force which can be detected, the largest electromotive force which may be amplified without distortion, the amplification factor between these limits, and the frequency range over which the amplifier is satisfactory. A knowledge of the smallest electromotive force which can be detected is of considerable interest. An amplifier giving a high overall amplification accompanied by loud disturbance from Schrott effect, mechanical vibration, interference from neighbouring electrical circuits, etc., may be inferior to an amplifier having a lower

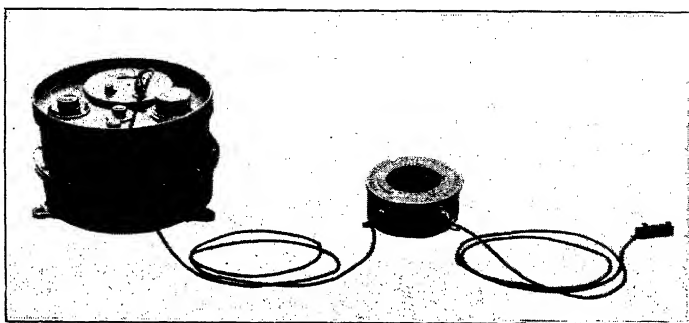


Fig. 5. The complete instrument.

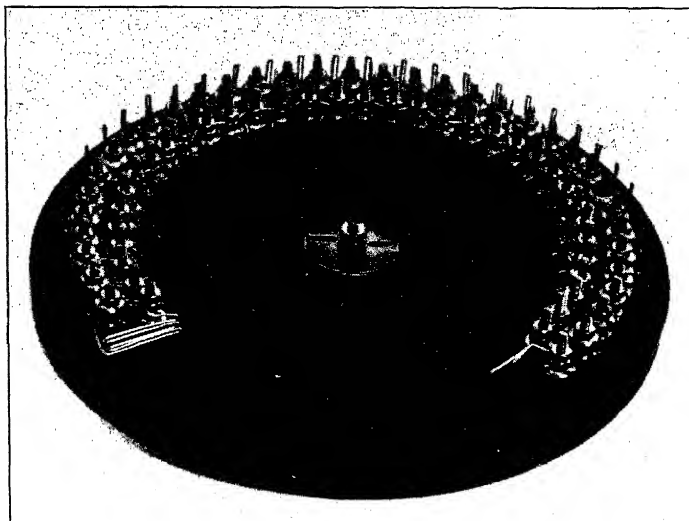


Fig. 6. Wiring of the artificial line.

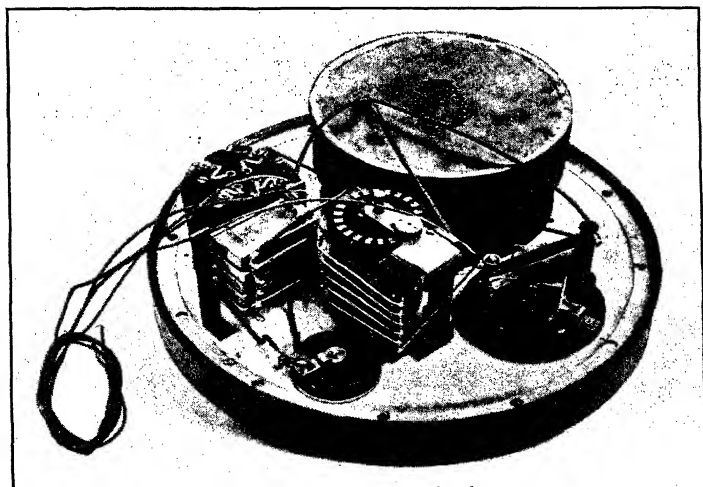


Fig. 7. Interior of valve oscillator.



overall amplification, but which is comparatively free from disturbances. A measurement of the minimum electromotive force required to produce an audible signal may be made by the arrangement of circuits shown in Fig. 1. One observer depresses the signalling key at irregular intervals and reduces the magnitude of the injected electromotive force until another observer, listening with the telephones, fails to hear the signals. The best settings for heterodyne, filament current, anode voltage, reaction, etc., are easily found by the same procedure. The overall amplification is measured by replacing the telephone with a measuring circuit of the same impedance and observing the deflections which correspond to known electromotive forces, injected into the circuit by depressing the signalling key. The contribution to the total amplification made by each stage of high frequency amplification may sometimes be measured by injecting an electromotive force in all the grid circuits in turn and observing the corresponding amplified electromotive forces.

If the electromotive force, injected into the circuit by depressing the signalling key, as shown in Fig. 1, is increased in strength, the amplified electromotive force is found to increase correspondingly until the last valve begins to produce distortion. Further increase in the injected electromotive force at first produces an increase in the amplified signal and then a decrease. Measurements of this kind are valuable in that they indicate the range in which an amplifier may be used without producing distortion. Many similar measurements with amplifiers for which the instrument is suitable will suggest themselves to those who are familiar with the technique of high frequency alternating current.

#### § 6. USE FOR THE MEASUREMENT AND COMPARISON OF THE STRENGTH OF SIGNALS

The instrument is well adapted for the measurement of the strength of wireless signals of long wave-length. The receiving circuit, shown to the right of Fig. 1, becomes a receiving circuit for wireless waves if a frame aerial is substituted for the coil in the tuned circuit. On depressing the signalling key, an artificial wireless signal is produced which can be adjusted in frequency magnitude and duration until it matches the true wireless signal very closely. It is not possible to match exactly because the strength of the artificial wireless signal can only be varied in steps. In a previous section, it is shown that the electromotive forces which are available form a geometrical progression in which the ratio between successive terms is  $1/\sqrt{2}$ . It is therefore possible to find a known electromotive force not differing by more than 20 per cent. from any unknown electromotive force within the range 15,000 to 0.0076 microvolts. A measurement of an unknown electromotive force is made by comparing it with two known electromotive forces, one slightly stronger and the other slightly weaker. The comparison may be made by listening to the artificial and the true signals with head telephones with an error of less than 10 per cent., even when considerable interference from atmospherics, etc., is present. If a more accurate measurement is desirable, a recording or indicating instrument is substituted for the head telephones.

## § 7. CONCLUSION

Several of these instruments have been in continual use for over a year and have been found to be robust, easily portable and reliable.

The authors desire to express their indebtedness to the Admiralty for granting permission to publish this paper and their appreciation of the assistance given by Mr H. Bellars and Mr L. O. Cook, of the Admiralty Research Laboratory, in the mechanical design and construction of the instrument.

## REFERENCES

- (1) A. G. JENSEN. "Portable Set for Field Strength Measurements." *Proc. Inst. Radio Eng.* **14**, 333-344 (1926).
- P. BORAS. "Field Strength Measurements in S. America." *Onde Elec.* **5**, 284-295 (1926).
- H. T. FRIIS and E. BRUCE. "A Radio Field Strength Measuring System for Frequencies up to 40 Megacycles." *Proc. Inst. Radio Eng.* **14**, 507-519 (1926).
- R. L. SMITH-ROSE. "On the Electro-Magnetic Screening of a Triode Oscillator." *Proc. Phys. Soc.* **34**, pt 4, 127 (1922).
- R. H. BARFIELD. "Some Experiments on the Screening of Radio Receiving Apparatus." *I.E.E. Journal*, **62**, 249 (1924).
- J. HOLLINGWORTH. "The Measurement of the Electric Intensity of Received Radio Signals." *I.E.E. Journal*, **61**, 501 (1923).
- J. HOLLINGWORTH. "A New Universal Long Wave Radio Intensity Measuring Set." *Journ. Sci. Instr.* **5**, 1 (1928).
- (2) G. ANDERS. "Quantitative Empfangsmessungen in der Funktelegraphie." *Elektr. Nachr. Technik*, **2**, Heft 12, 401-425 (1925).
- (3) D. W. DYE. "Current Transformed Methods of Producing Small Known Voltages and Currents at Radio Frequencies for Calibrating Purposes." *Proc. Inst. Elec. Eng.* **63**, 597 (1925).

## DISCUSSION

Mr R. S. WHIPPLE: I should like to congratulate the authors on the very practical apparatus they have designed. It is an extremely difficult matter to achieve such effective screening.

Dr D. OWEN: The authors offer a solution of an important practical problem in high-frequency testing. The all-important point, however, as to the adequacy of their artificial line to supply voltages according to a simple exponential law is not treated theoretically in the paper. It seems desirable that this basic assumption should be justified, say, by reference to some publication containing a full examination of the point. The steps taken, with such success, to avoid leakage of magnetic and electric fields are of much interest. The method of eliminating stray field due to the toroid is notable in that it recognises the fact—usually quite overlooked—that the current in the winding will not only produce circular magnetic lines within its interior, but also generate a field outside, in virtue of its acting as a one-turn coil coincident with a central line within the toroid. This is, of course, true of every solenoidal helical winding, which is thus not the complete equivalent of the mathematical current sheet of theory.

Dr W. H. ECCLES: Workers in my laboratory in the early days of amplifiers found it necessary to take extreme precautions in screening the oscillator used for supplying the current to be amplified by the instrument under test. Complete enclosure in metal did not seem good enough, so the amplifier was placed in another room and the leads coming from the oscillator were carried through "compo" piping. It was found necessary to close up all gaps in the piping. Even then stray disturbance direct from the oscillator was not all eliminated. Instead of an artificial line I used a calibrated variable mutual inductance and a potentiometer in which the resistance was a liquid electrolyte. I experienced difficulty from the fact that tapping the potentiometer disturbs the voltage distribution in the potentiometer circuits, especially when the impedance of the tapping circuit was low. Have the authors considered this difficulty in their use of an artificial line?

Mr R. M. WILMOTTE (communicated): The authors are to be congratulated on the very ingenious method they have devised to obtain a range of E.M.F. whose extremes are in the high ratio of  $2 \cdot 10^6$  to 1. An artificial line for the purpose is far more satisfactory than a potentiometer for, while the latter's scale is linear, the former's is logarithmic. There is, moreover, the considerable advantage that the input impedance of the line is extremely low and capacity effects correspondingly negligible. The greatest of these capacity effects is, no doubt, the input impedance of the amplifier. The authors suggest replacing the resistance elements by inductances for higher frequencies. I should think that the design of such a line with the elimination of mutual inductances would be extremely difficult, especially as the decrement of these inductances as well as their impedances would have to be low (if capacity effects are to be neglected). The difficulty with both resistances and inductances is that, owing to impurities, they vary with frequency. The purest form of impedance available is a condenser. I should be very interested to hear the authors' views on the possibility of using large condensers instead of either resistances or inductances for high frequencies. Except at extremely high frequencies, the inductances could be made negligible while capacity-to-screen effects could readily be taken into account in the design, even though the impedance of the line were large. The minimum size of condenser that could be used would be dependent on the input impedance of the amplifier. It might be necessary to bring the line on to the lower part of the resonance curve in order to obtain a measurable current in the thermo-ammeter, but there would be no great objection to this. If this produced too large voltages, the artificial line could be connected to a capacity potentiometer (two condensers in series, the line being connected across the larger one). As a small point of interest, I would like to know why a screen for the electric field is used between the primary and secondary of the toroid.

AUTHORS' reply: The description which Dr W. H. Eccles has given of the difficulties which he encountered in measuring the sensibility of an amplifier and the methods he adopted to overcome them are of great interest. His experimental screened cable in which two insulated wires were run through a lead or "compo"



pipe could hardly be improved upon, its only disadvantage being its limited flexibility. The liquid electrolyte as a non-inductive potentiometer would be very satisfactory provided that the circuit into which it was introduced had a sufficiently high resistance. The artificial line described in the paper was wound to a low resistance of about 0.1 ohm so that only a circuit of exceptionally low resistance would disturb it.

We are unable to give Dr D. Owen a reference to a publication in which the theory of the artificial line as a means of producing small known electromotive forces is specifically presented. However, it is a special case of the electrical filter circuit, the generalized theory of which has been given in numerous publications, references to some of which follow:

(1) Campbell, *Bell System Technical Journal* (Nov. 1922). (2) Zobel, *ibid.* (Jan. 1923). (3) Zobel, *ibid.* (Jan. 1925). (4) Peters, *Journ. A.I.E.E.* **42**, 445 (1923). (5) Peters, *Phil. Mag.* **6**, no. 34 (1928). (6) Peters, *ibid.* **3**, no. 16 (Supplement) (1927).

The properties of the artificial line can be inferred from first principles by the application of Kirchhoff's equations for electrical networks. If  $Z_1$  be the complex impedance of a series element and  $Z_2$  the complex impedance of a shunt element, the ratio,  $\alpha$ , of the current in the  $(n + 1)$ th shunt element to that in the  $n$ th element is given by the equation

$$1/\alpha + \alpha = 2 + Z_1/Z_2.$$

In general,  $\alpha$  is a complex quantity from which the decrement of the artificial line and the change of phase per section can be inferred. The decrement of an artificial line whose shunt and series elements are any combination of resistance, capacity and inductance can be found by solving the above equation. The calculated decrement of the artificial line must usually be verified by a calibration against some precision method of producing small known electromotive forces. The method described by Dr D. W. Dye to which a reference has been given is very suitable for this purpose.

Mr R. M. Wilmotte has summarized the advantages of the artificial line very concisely. The range of electromotive forces which must be measured in the testing of valve amplifiers is so large that a measuring instrument with a logarithmic scale is very desirable. His objection to our suggestion of an artificial line for high frequencies, in which both series and shunt elements would be inductances, is that residual mutual inductances between adjacent sections of the line would introduce errors however carefully the line were constructed. Provided however that a few sections at the beginning and end of the line were avoided, the greater part of such a line would have a constant decrement per section. A calibration of the line would be necessary. Mr Wilmotte's alternative of a line with condensers for series and shunt elements seems quite practicable and has, as he points out, marked advantages at very high frequencies. The electric screen between the two windings of the toroidal transformer seems superfluous theoretically but is found experimentally to be essential.

## THE EFFECT OF MOIST AIR ON THE RESISTANCE OF PENCIL LINES

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College, Lahore.

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**ABSTRACT.** The resistance of a pencil line is found to increase when it is kept in a moist atmosphere. The change in resistance for different degrees of moisture is investigated and a suggestion is made that this change may, in certain circumstances, be utilised to measure humidity.

**D**URING a measurement of the resistance of a pencil (carbon) line by the Wheatstone bridge method it was observed that the presence of moisture in the air caused a gradual increase in the resistance of the line. The object of the present investigation was to study the changes in the resistance of a line when it was subjected to a series of humidity changes and to see how far this property could be utilised for measurements of humidity.

The resistance of the various lines used was of the order of 0.1 megohm. Appropriately high resistances formed the other three arms of the bridge. Instead, however, of balancing every time to find the absolute resistance of the carbon line, the null position was obtained once only at the beginning of each series of experiment and the change in the resistance of the line under the changing conditions obtained by noting the galvanometer deflections round about the null point, the equivalence between deflection and change in resistance being known by a previous calibration.

The pencil lines were drawn on rectangular pieces of ground glass or of ebonite, the surface of the latter having been roughened by means of emery paper, previous to the drawing of the lines on them. The ends of the lines were broadened out and tinfoil-covered rubber pieces were used to secure good contact at the ends. The line under experiment was kept inside a wide glass tube through which could be passed a current of dry or moist air by means of a suitable aspirator arrangement. The air was dried by passing it through calcium chloride tubes or by allowing it to bubble through concentrated sulphuric acid. The humidity of the moist air was controlled by means of suitable sulphuric acid-water solutions.

A current of air (dry or moist) was blown through the tube for a given time and changes in the resistance of the line were measured after regular intervals of time. Before the change due to a given humidity was measured the line was exposed to a current of dry air for at least half an hour and the change in its resistance determined every few minutes. Air after bubbling through a sulphuric acid-water

solution of known strength (from which the humidity of the outgoing air could be calculated) was then passed through the tube containing the line, and the changes in the resistance measured for 25 minutes. Dry air was again passed for half an hour or more before subjecting the line to the influence of moist air of a different humidity, and so on.

The resistance of the line changes also with temperature and with time. The temperature variation, while the line was subjected to one particular humidity or to a current of dry air, was never more than about a fifth of a degree centigrade; and since the temperature coefficient of the resistance was approximately  $2 \times 10^{-3}$  this caused a change in the given resistance of only about 1 in 2500. As regards the change of resistance with time, it was found that with a freshly prepared line the change per hour was of the order of 1 in 10,000 in the beginning. This reduced to about 1 in 20,000 after 20 days, and to 1 in 100,000 after 35 days. These changes can therefore be regarded as negligible for our present purposes.

When a current of moist air is passed over one of these lines, which has been previously exposed to a current of dry air, its resistance rises at first rapidly and then more slowly, attaining a sort of saturation value in about 25 minutes. On subjecting the line to the influence of dry air at this stage the resistance falls fairly rapidly. In the case of ground glass, it was observed that the line on being exposed to rather high humidities showed, at first, the increase of resistance, but then a decrease. The latter was found to be due to the moisture condensed on the glass, which caused a lowering of the insulation resistance of the glass itself. On coating the portion of the glass outside the line with a thin layer of wax the above mentioned anomalous behaviour disappeared. Such a pencil line (i.e. a line on a ground glass piece the surface of which, outside the line, is waxed) is, therefore, the one suitable for our purposes. With a line on an ebonite piece there is no such trouble.

For a line on ebonite the change of resistance in the first 25 minutes was nearly 1 in 50 when the absolute humidity was 42 mm. and about 1 in 250 for a humidity of 26 mm. In the case of waxed ground glass the changes are more than twice as great. At rather low humidities (below 26 mm. for ebonite and below 10 mm. for waxed ground glass) the resistance showed either a gradual fall from the very beginning or a steady value. The changes in resistance are of course different for different lines, but they are nearly the same for the same line under similar conditions.

The curves in Fig. 1 represent the change of resistance with time for different humidities when the line was on ebonite. The curves in Fig. 2 are for a line on waxed ground glass. As previously indicated the humidity portion of the curves rises rapidly at first and then more slowly. The drying curves show a fall much more abrupt than the rise in the humidity curves. The portions of the curves corresponding to drying become nearly horizontal after about 20 minutes.

The phenomenon of a slow gradual increase of resistance of pencil lines with time, and a much more rapid increase when the line is exposed to moist air, seems to be due to air and water vapour particles finding their way into the interstices of

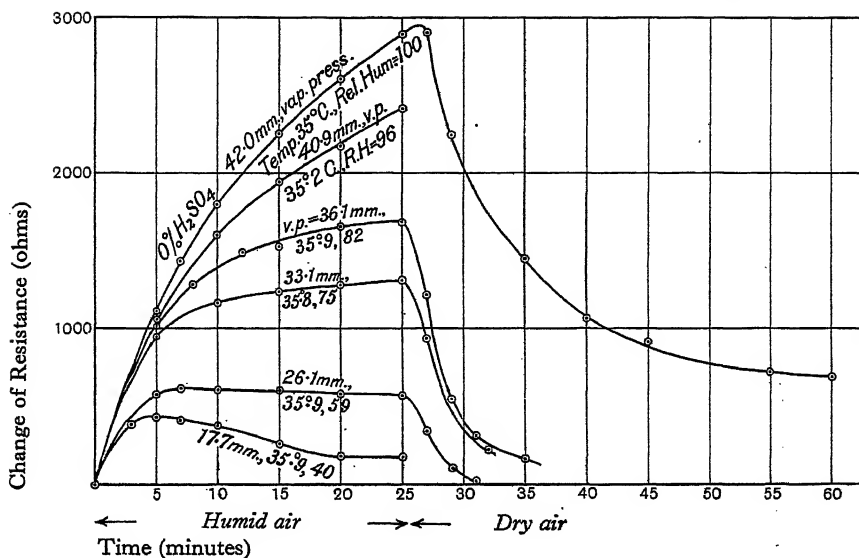


Fig. 1. Change in resistance of line on ebonite.

## DATA FOR THE CURVES IN FIG. 1

Line on ebonite. Initial resistance = 155,100 ohms

Time (min.)	0	5	7	10	15	20	25	} $\frac{0}{\%}$ $\text{H}_2\text{SO}_4$ or $\text{H}_2\text{O}$ V.P. = $42.0$ mm. T. = $35.0^\circ\text{C}$ . R.H. = $100$	
Change of Res. (ohms)	0	1104	1436	1796	2256	2604	2896		
Time	27	29	35	40	45	55	60	} D.T. = $35.0^\circ\text{C}$ .	
Change of Res.	2904	2240	1448	1064	912	728	692		
Time	0	5	10	15	20	25		} V.P. = $40.9$ mm. T. = $35.2^\circ\text{C}$ . R.H. = $96$	
Change of Res.	0	1052	1600	1940	2168	2404			
Time	0	5	8	12	15	20	25	} V.P. = $36.1$ mm. T. = $35.9^\circ\text{C}$ . R.H. = $82$	
Change of Res.	0	1012	1280	1472	1524	1654	1688		
Time	27	29	31	35				} D.T. = $35.8^\circ\text{C}$ .	
Change of Res.	1212	542	308	158					
Time	0	5	10	15	20	25		} V.P. = $33.1$ mm. T. = $35.8^\circ\text{C}$ . R.H. = $75$	
Change of Res.	0	952	1160	1228	1272	1309			
Time	27	30	32					} D.T. = $35.8^\circ\text{C}$ .	
Change of Res.	930	422	218						
Time	0	5	7	10	15	20	25	} V.P. = $26.1$ mm. T. = $35.9^\circ\text{C}$ . R.H. = $59$	
Change of Res.	0	578	608	604	600	578	570		
Time	27	29	31					} D.T. = $35.9^\circ\text{C}$ .	
Change of Res.	342	100	16						
Time	0	3	5	7	10	15	20	} V.P. = $17.8$ mm. T. = $35.9^\circ\text{C}$ . R.H. = $40$	
Change of Res.	0	396	438	416	376	264	180		174

V.P. = vapour pressure; T. = temperature; R.H. = relative humidity; D.T. = drying temperature.

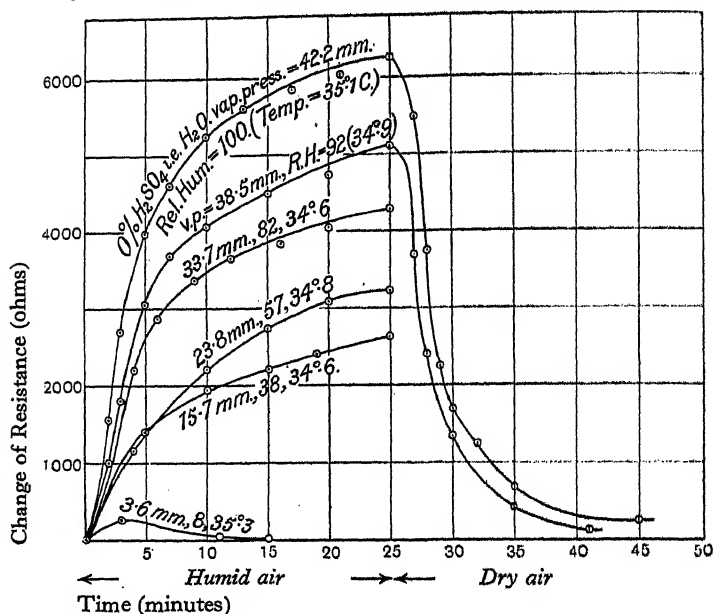


Fig. 2. Change in resistance of line on waxed ground glass.

## DATA FOR THE CURVES IN FIG. 2

Line on waxed ground glass. Initial resistance = 120,000 ohms

Time (min.)	0	2	3	5	7	10	13	$\left. \begin{array}{l} 0\% \text{ H}_2\text{SO}_4 \text{ or H}_2\text{O} \\ \text{V.P.} = 42.2 \text{ mm.} \\ \text{T.} = 35.1^\circ \text{ C.} \\ \text{R.H.} = 100 \\ \text{D.T.} = 35.2^\circ \text{ C.} \end{array} \right\}$
Change of Res. (ohms)	0	1570	2708	3958	4610	5245	5600	
Time	17	21	25					
Change of Res.	5853	6045	6255					
Time	27	28	29	30	32	35	45	$\left. \begin{array}{l} \text{V.P.} = 38.5 \text{ mm.} \\ \text{T.} = 34.9^\circ \text{ C.} \\ \text{R.H.} = 92 \\ \text{D.T.} = 35.0^\circ \text{ C.} \end{array} \right\}$
Change of Res.	5482	3730	2258	1682	1245	685	230	
Time	0	2	3	5	7	10	15	
Change of Res.	0	1000	1812	3062	3672	4077	4500	
Time	20	25						$\left. \begin{array}{l} \text{V.P.} = 33.7 \text{ mm.} \\ \text{T.} = 34.6^\circ \text{ C.} \\ \text{R.H.} = 82 \\ \text{D.T.} = 35.0^\circ \text{ C.} \end{array} \right\}$
Change of Res.	4732	5102						
Time	27	28	30	35	41			
Change of Res.	3662	2412	1332	417	129			
Time	0	2	3	4	6	9	12	$\left. \begin{array}{l} \text{V.P.} = 33.7 \text{ mm.} \\ \text{T.} = 34.6^\circ \text{ C.} \\ \text{R.H.} = 82 \end{array} \right\}$
Change of Res.	0	1280	1855	2205	2870	3355	3653	
Time	16	20	25					
Change of Res.	3846	4046	4295					
Time	0	4	10	15	20	25		$\left. \begin{array}{l} \text{V.P.} = 23.9 \text{ mm.} \\ \text{T.} = 34.8^\circ \text{ C.} \\ \text{R.H.} = 57 \end{array} \right\}$
Change of Res.	0	1164	2197	2742	3072	3224		
Time	0	2	5	10	15	19	25	
Change of Res.	0	658	1416	1956	2214	2404	2634	
Time	0	3	11	15				$\left. \begin{array}{l} \text{V.P.} = 3.6 \text{ mm.} \\ \text{T.} = 35.3^\circ \text{ C.} \\ \text{R.H.} = 8 \end{array} \right\}$
Change of Res.	0	260	35	20				

V.P. = vapour pressure; T. = temperature; R.H. = relative humidity; D.T. = drying temperature.

the line. The latter is not a continuous unbroken chain of carbon particles, but is made up of grains of carbon lying side by side, the contact between them not being perfectly rigid. The particles of air or vapour ensconce themselves in between the grains of carbon, thus increasing the resistance of the line. From the appearance of the curves in Figs. 1 and 2 (remarked at the end of the last paragraph), it would

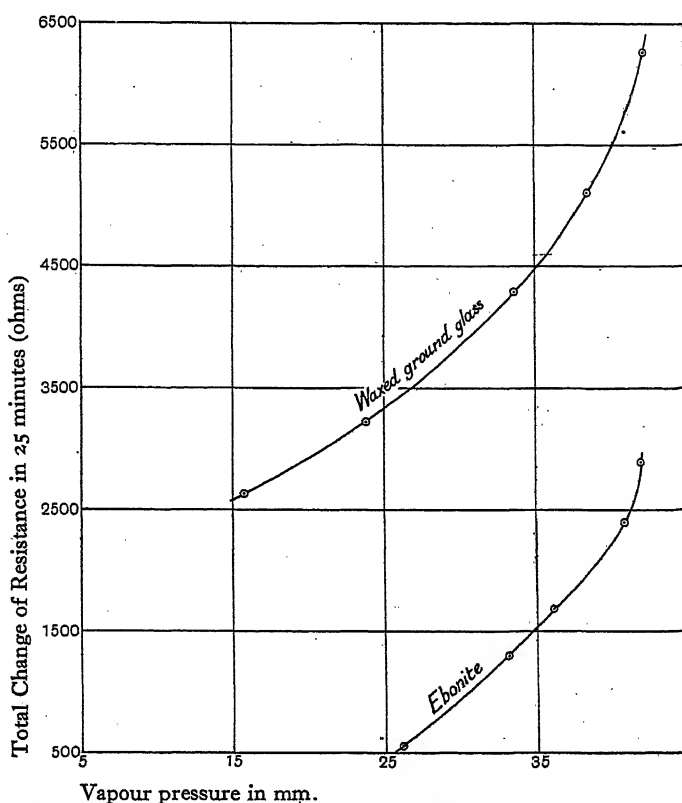


Fig. 3. Relation between change of resistance and humidity of air.

DATA FOR THE CURVES IN FIG. 3

Vapour pressure (mm.)	26.1	33.1	36.1	40.9	42.0	} Ebonite
Total Change of Resistance in 25 min. (ohms)	570	1309	1688	2404	2896	
Vapour pressure (mm.)	15.7	23.8	33.7	38.5	42.2	} Waxed ground glass
Total Change of Resistance in 25 min. (ohms)	2634	3224	4295	5102	6255	

appear that the rate at which vapour particles find their way into the interstices of a previously dried pencil line is slower than the rate at which they are dislodged by a current of dry air.

The curves in Fig. 3 show the relation between the absolute humidity of the air (saturation humidity being 42.0 and 42.2 mm. for ebonite and waxed ground glass lines respectively) and the changes in the resistance it causes in 25 minutes for lines on ebonite and waxed ground glass. They are fairly smooth and may be

used for determining the humidity of air. As an example, air was passed through the tube containing a line on ebonite, after first bubbling through a given sulphuric acid-water solution, and the corresponding change of resistance in 25 minutes was measured. (Dry air was passed through the tube for 30 minutes before passing the specimen air, as required by the conditions of the experiment.) The change in resistance was found to be 852 ohms and from the curve for ebonite in Fig. 3 we find that this corresponds to an absolute humidity of 29.0 mm. The density of the solution, as found by a hydrometer, was 1.27, corresponding to a concentration of about 35 per cent. acid, and a vapour pressure of 28.3 mm. The agreement between the two results is within 3 per cent., which appears to be very promising. A further study of the problem will perhaps enable us to attain a higher degree of accuracy.

At this early stage of the study of the subject it appears that the method will not be suitable when the absolute humidity of the air is less than about 26 mm. for a line on ebonite and about 10 mm. for one on waxed ground glass. The method also seems unsuitable, so far, for measuring the humidity of the atmosphere at any particular time, but can only be used to measure the mean humidity during a certain period of time. Also, since the resistance of pencil lines does not remain constant for a long period, the apparatus may require occasional calibration by passing known humidities over the line and noting the changes in its resistance.

These are some of the difficulties and limitations which would appear, at least at this early stage, to militate against the use of carbon lines for hygrometric purposes. Future experimentation on the subject may, however, overcome the difficulties. The much more abrupt fall of the drying curves as compared to the comparatively slow rise of the humidity curves might, for instance, be regarded as showing that the results obtained from the drying curves (after an exposure of the line to moist air) will probably be more useful than those from the humidity curves for hygrometric determinations.

## DISCUSSION

Dr S. G. BARKER, Woollen and Worsted Research Association (communicated): As one of those who are compelled to wear an electrical aid for hearing, some time ago I noted that my instrument was specially sensitive to changes in atmospheric humidity. Whereas I was able to hear perfectly whilst in a warm, dry room, on emerging into another room where the humidity was higher, I could detect a very great diminution in the efficiency of the instrument. On a rainy day it was practically impossible to use the instrument in the open air. This led me to think that there must be some intimate relation between the resistance of the carbon granules in the microphone and the humidity of the atmosphere in which the instrument was used. I therefore carried out a series of experiments in air at different humidities.

When one is slightly deaf, the ear seems to become very sensitive to even small changes in the volume of the sound, and although to the normal person this volume

seems to be hardly fluctuating at all, yet to the deaf person even these small diminutions are a matter of great moment, making all the difference between audibility and inaudibility.

It struck me that variations in humidity might explain the packing of telephone transmitters in which carbon granules are used. I found that after a time the carbon granules get covered with a dust, caused by their continually rubbing against each other, and that this dust is particularly sensitive to humidity. I have been working recently with carbon granules both in a tube and in an open trough, in order to devise a new method of humidity control and measurement, and I see from the paper that I am largely anticipated in this regard. The paper, therefore, has a greater significance than perhaps the authors recognise, in that the effect of humidity on the resistance of carbon granules is closely connected with their tendency to packing in microphones and particularly those which are used for aural aids for the deaf.

I might mention that the effect of humidity on the diminution of sound is practically instantaneous. At any rate the time lag is very small.

The efforts made so far to construct an instrument for the control or measurement of humidity have met with a fair amount of success, but are very incomplete. It is hoped that in the near future we may be able to make further progress with the instrument in our laboratories, but I felt that these remarks should be made on this paper to indicate that other workers besides the authors have been in the field.



# AN ABSOLUTE CURRENT-BALANCE HAVING A SIMPLE APPROXIMATE THEORY

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AND OTHER STUDENTS OF WESTMINSTER TRAINING COLLEGE

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**ABSTRACT.** A simple form of current balance has been constructed which, when tested by experimental comparison with a standard ohm and Weston cell, measures currents with a probable error of about 1 part in 1000. The calculation of the force acting on the moving coil of the balance involves no pure mathematics beyond that of the Intermediate B.Sc. The coils are single layers so that they can in the future be made as precise helices. Actually we have had to aim at cheapness rather than at perfection, and so irregularities of shape leave the current uncertain by 5 parts in 1000. A second approximation, depending on a simple deduction from Laplace's equation, corrects the elementary theory by 1.4 in 1000 of current.

## § 1. PURPOSE

"ABSOLUTE MEASUREMENTS" are on the syllabus of the University of London for the General B.Sc. in Physics. The current balance is the most important instrument for the absolute measurement of current. But the theory of the balance at the N.P.L. involves elliptic integrals, and these are beyond the syllabus in pure mathematics for the B.Sc. aforesaid. These considerations have impelled us to make an instructional instrument. Dr F. E. Smith\* has already made a simple instrument; but as our arrangement is very different, it may be worth describing.

## § 2. SIMPLE THEORY

The desired simplification of the theory has been attained by lengthening the coils in comparison with their diameter. The moving coils of Rayleigh and Mrs Sidgwick were narrow rings†. Those of the N.P.L. instrument (1907) have a length about 0.65 of their diameter. In the present instrument the length of the coils is five or six times their diameter.

The outer coils are placed in contact end to end, so that the direction of the magnetic force due to the two outer coils is that shown by the arrows in Fig. 1. The coils have a common axis, which is vertical. The inner coil hangs from the balance-beam.

Now by general theory the force which we weigh is  $\partial W / \partial z$  where  $W$  is the mutual energy of the currents and  $z$  is the vertical displacement of the inner coil.

Let suffix 1 refer to the fixed coils considered as one system, while 2 is suffix for the movable coil. Let the current in all coils be  $j$ .

\* F. E. Smith, Phys. & Opt. Soc. Exhibition, Jan. 1926, Catalogue B 8.

† See A. Gray, *Absolute Measurements in Electricity and Magnetism*, 1921, Ch. XII.

Then  $W = j \left\{ \begin{array}{l} \text{Number of linkages with coil 2 of tubes of induction} \\ \text{produced by coil 1} \end{array} \right\} \dots\dots(1).$

Hence  $\frac{\partial W}{\partial z} = j \left\{ \begin{array}{l} \text{Change in aforesaid linkages per centimetre axial} \\ \text{displacement of inner coil} \end{array} \right\} \dots\dots(2).$

As Fig. 1 shows, the tubes of induction, which enter the inner coil by both ends, escape through its central portion. Let  $H_1$  denote the magnetic intensity due to the outer coils at a point  $P$  on the axis at the "end" of the inner coil. Then, as is well known,

$$H_1 = 2\pi n_1 j_1 \{ \cos \theta_A - \cos \theta_B - \cos \theta_C + \cos \theta_D \} \dots\dots(3),$$

where  $n_1$  is the number of turns per centimetre in the fixed coil, and  $\theta_A, \theta_B, \theta_C, \theta_D$  are the semivertical angles of the cones subtended at  $P$  by the four "ends" of the outer coil taken in succession so that  $A$  is the near end,  $B$  and  $C$  are close together in the middle and  $D$  at the far end. See Fig. 1. The "end" of a helix is regarded as a plane normal to the axis through the mid point of the last turn.

The sizes of the coils were so chosen that, at the ends of the inner coil,

$$\frac{\partial H_1}{\partial z} = 0 \dots\dots(4),$$

which, on omitting non-vanishing factors, is equivalent to

$$0 = (\sin \theta_A)^3 - (\sin \theta_B)^3 - (\sin \theta_C)^3 + (\sin \theta_D)^3 \dots\dots(5).$$

Thus the ends of the inner coil are in almost uniform fields  $H_1$ . The total number of tubes of induction entering the inner coil, of radius  $r_2$ , by its two ends is

$$2\pi r_2^2 H_1 = N, \text{ say, } \dots\dots(6),$$

and  $N$  is practically unaffected by axial displacements of a centimetre. Condition (5) means that the force does not vary while the balance swings. The antisymmetrical form of the outer current does not help in this.

Let  $n_2$  denote the number of turns per centimetre of axial length of the inner coil. When this coil is displaced axially by one centimetre then each of the  $N$  magnetic tubes escaping through its walls is cut by  $n_2$  turns of wire. Hence

$$(\text{force weighed}) = \frac{\partial W}{\partial z} = j n_2 N = 2\pi j n_2 r_2^2 H_1 \dots\dots(7).$$

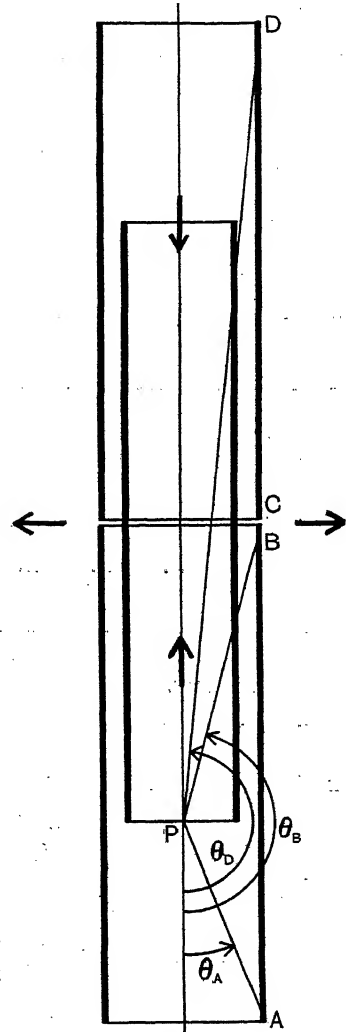


Fig. 1.

Finally if  $2m$  grams are needed to balance reversal of the current-connexion between the coils

$$j^2 = \frac{mg}{4\pi^2 n_1 n_2 r_2^2 \{\cos \theta_A - \cos \theta_B - \cos \theta_O + \cos \theta_D\}} \dots\dots(8).$$

### § 3. CONSTRUCTION AND LENGTH MEASUREMENTS

The foregoing design was embodied as an instrument by Mr V. Stanyon, B.Sc., who solved equation (5), made coils to satisfy that condition, and with Mr G. W. Roe mounted them in position. The inner coil was wound on a bakelite tube, the outer on a tube made for the purpose by rolling up a large sheet of glued cartridge paper. The diameters were measured by a large slide caliper made by Troughton and Sims and checked for the outer coil by a steel tape (Rabone). The axial lengths were measured by a cathetometer (Pye) and a metal scale (Chesterman). In these measurements Messrs V. Stanyon, H. F. O. Dawes, C. C. Prior and W. L. Vasey took part, and the measurements were repeated or checked by L. F. Richardson. The following table shows the means.

Table I: Design of coils.

	Outer	Inner
Axial length between mid planes of end turns, cm.	66.8 <sub>8</sub>	40.2 <sub>2</sub>
Radius of cylinder through axis of wire, cm. ...	5.45 <sub>9</sub>	3.845 ± 0.001
Turns per centimetre of axis ... ..	12.8 <sub>3</sub> *	8.27 <sub>8</sub>
Diameter of copper wire, cm. ... ..	0.06 <sub>3</sub>	. 0.05 <sub>6</sub>
Insulation ... ..	over enamel Enamel and cotton, shellaced	Double silk, shellac and celluloid

\* Mean of two decimetre portions near ends of inner coil. Middle only 12.53, general mean about 12.7.

It is found from these measurements that

$$\theta_A = 22^\circ 18'.5, \theta_B = 180^\circ - 15^\circ 12'.3, \theta_O = 180^\circ - 15^\circ 8'.9, \theta_D = 180^\circ - 5^\circ 49'.2,$$

$$\cos \theta_A - \cos \theta_B - \cos \theta_O + \cos \theta_D = 1.860,$$

Messrs S. O. Myers, D. J. Proctor, W. Toyne and L. F. Richardson agreeing in 1.860.

Hence formula (3) gives the intensity at the centre of the end of the inner coil when 1 ampere flows in the outer coil as

$$H_1 = 14.99 \text{ gauss} \dots\dots(9).$$

Hence, from (8), as  $g = 981.2 \text{ cm. sec.}^{-2}$ ,

$$2m = 235.0 j^2 \text{ when } j \text{ is in E.M.U.}$$

That is to say for one ampere the mass to balance reversal would, from length measurements, be 2.35<sub>0</sub> grams, according to this first approximation .....(10).

The flexible leading wires to the suspended coil are No. 43 s.w.g. tinned copper, one strand sufficing each way.

The resistance of the instrument is about 34 ohms.

The balance was obtained from Messrs F. E. Becker, London, who list it as carrying 300 grams, with a sensitivity of 3 to 4 milligrams, and a price of £3. 7s. 6d. The stirrups at the ends of the beam have arrestments; without these we have had trouble. The beam lengths agree to 1 in 10,000. The balance is in a glass case; the coils in a cupboard underneath.

#### § 4. BEHAVIOUR

It was found at once that the weight to balance reversal of one ampere was about 2.3 grams so that predictions were roughly correct; but the following three difficulties had to be met:

(i) The suspended system decreased in weight during a run. Not all of this decrease was regained on cooling. So presumably the permanent part is due to evaporation, the temporary part to rising air-currents and to softening of the leading-in wires. The effect was as much as 0.1 or 0.2 gram. The observations were arranged so as to eliminate it by allowing an hour or more for preliminary warming, by repeated reversal of the current in one coil only, and by weighings made at observed times.

(ii) The oscillations of the balance were at first irregular, when the coils were connected to accumulators. Thus, choosing as example an unusually violent disturbance, successive turning points were

13.3      17.0      15.5  
8.4      8.6      9.9

This effect is probably due to an accumulation of hot air in the coils coming out in a sudden upset, instead of in a steady flow. This happened when the outer tube was closed below and open above. After fitting a lid to the outer tube, oscillations were much steadier, successive turning points being for example

13.5      13.0      12.6      12.1      11.8      11.5      11.3  
9.5      9.6      9.8      9.9      9.9      10.0      10.2

(iii) Fluctuations of  $\pm 0.001$  ampere in the current persisted. Opening the door of the coil-case increased the current suddenly by more than 0.003 ampere; so it is probable that the fluctuations are due to eddying air currents cooling the coils. Accordingly the current was adjusted frequently, and a record kept of its wandering.

#### *Specimen observation*

1928 Sept. 17. Current flowing for 4 hours before weighings began. The current was adjusted until the drop of potential across 1 ohm just balanced a standard cell, momentarily put in circuit by a tapping key. Standard Resistance, Tinsley No. 15,521 to carry 3 amperes, oil cooled, certified by the makers to be 1.0001 ohms at 26° C. Standard Cell, by Cambridge Inst. Co., certified by N.P.L. to give 1.0183 international volts at 20° C. One cm. motion of the galvanometer-spot corresponded to a change of  $10^{-4}$  ampere.

Observer L.F.R.

Table II: Variation of readings with time.

Time mins.	Temp. of ohm	Galv. deflection cm.	Switch	Weight in pan grm.	Turning points			Centre of oscil.	Weight to centre
2	—	0, + 5	→	13.33	6.6	11.6	6.6	9.1	13.322
5	25.7	0, - 3	→	13.32	15.0	5.8	14.4	10.2	
9?	—	0, + 8	←	10.88	6.2	14.2	6.0	9.9	10.879
12	25.8	0, ± 3	←	10.87	12.7	7.2	13.1		
17	—	0, - 4	→	13.31	7.0	12.5	7.2	10.7	13.303
20	—	± 5	→	13.30	13.1	8.1	13.3		
24	25.8	± 3, + 3	←	10.86	8.2	13.0	8.7	9.3	10.857
26	—	± 2	←	10.85	13.9	4.8	13.7		
31	—	± 4, - 10	→	13.29	4.9	13.6	5.2	10.4	13.277
34	25.9	± 3	→	13.28	8.3	12.4	8.4		
39	—	± 3, - 2	←	10.84	12.2	8.3	12.2	9.8	10.835
41	—	± 2, - 4	←	10.83	11.4	8.6	10.9		
46	25.9	± 3, + 3	→	13.27	8.8	10.8	8.4	9.1	13.266
52	—	± 5, + 5	→	13.26	7.8	12.8	8.1		
					12.8	8.1	12.8	9.1	
					4.2	13.7	4.9	9.8	
					13.4	4.9	12.8	10.1	
					7.7	11.6	7.6	10.3	
					11.3	8.8	11.1	10.3	
					9.8	9.2	10.1	9.1	
					9.2	9.9	10.3	9.1	
					9.3	11.6	9.0	11.1	
					11.6	9.2	11.1	10.4	
					5.7	12.5	5.5	9.1	
					12.4	5.9	12.2	11.1	
					11.7	10.7	11.7	11.1	
					10.4	11.6	10.4	11.1	

Temperature of Weston cell 20°.8 C.

Temperature of standard cell 20°.6 C.

Now if we assume a steady drift of 1.4 milligrams per minute and correct all the weights to 24<sup>min</sup> we obtain

switch	→	13.292	13.294	13.288	13.300	13.293	Mean
	←	10.859	10.857	10.856	—	10.857	
Difference						2.436 ± 0.005 grm.	

The mean electric current was 1.0183/1.0001 international ampere. Therefore to balance reversal of one ampere required

2.350 grams.

Other observations made without a lid on the outer coil, were as follows:

Table III: Variation with time without lid on outer coil.

Date	Drift, milligrams per minute	Grams to balance reversal of one internat. ampere	Observers
Feb. 4	—	2.346	L. F. Richardson
Feb. 7	1.2	2.350	C. C. Prior and
Feb.	—	2.338	W. L. Vasey
Sept. 15	2.8	2.366	L. F. Richardson
	Mean	2.350	

# § 5. SECOND APPROXIMATION

Take rectangular coordinates  $x, y, z$ , the  $z$ -axis coinciding with the axis of the coils, and the origin being in the plane of the end of the inner coil. Let the magnetic intensity have components  $H_x, H_y, H_z$ .

The first approximation consisted in the assumption that  $H_z$  was uniform over the end of the inner coil. For the second approximation expand  $H_z$  in powers of  $x$  and  $y$  as far as the second degree. By symmetry the linear terms are absent, together with  $xy$ , so that

$$H_z = A + B(x^2 + y^2) \text{ in which } A \text{ and } B \text{ are independent of position} \dots\dots(11).$$

Let  $x^2 + y^2 = r^2$ . The flux of induction into one end of the inner coil, which has been denoted in (6) by  $N/2$  is therefore

$$\frac{N}{2} = \int_0^{r_2} H_z 2\pi r dr = A\pi r_2^2 + B2\pi \int_0^{r_2} r^3 dr = \pi r_2^2 A \left(1 + \frac{B}{2A} r_2^2\right) \dots\dots(12).$$

The value of  $A$  has already been found; see (3) and (6).

Now we can find  $B$  from a general property of the magnetic field. For, except in the electric current, a magnetic potential  $\phi$  exists such that

$$\frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial y^2} + \frac{\partial^2 \phi}{\partial z^2} = 0 \dots\dots(13),$$

and

$$H_z = -\partial \phi / \partial z \dots\dots(14).$$

Differentiating (13) with respect to  $z$

$$\frac{\partial^2 H_z}{\partial x^2} + \frac{\partial^2 H_z}{\partial y^2} + \frac{\partial^2 H_z}{\partial z^2} = 0 \dots\dots(15).$$

But by (11) we have

$$\frac{\partial^2 H_z}{\partial x^2} = \frac{\partial^2 H_z}{\partial y^2} = 2B \dots\dots(16).$$

So, from (15) and (16),

$$B = -\frac{1}{4} \frac{\partial^2 H_z}{\partial z^2} \dots\dots(17).$$

And  $\partial^2 H_z / \partial z^2$  can be found on the axis from (3) in which

$$\cos \theta = z(r_1^2 + z^2)^{-\frac{1}{2}} \text{ for each suffix } A, B, C, D \dots\dots(18),$$

$z$  being the distance of the appropriate end of the outer coil. Differentiating (18) twice with respect to  $z$ , and inserting in (3) it is found that

$$\frac{\partial^2 H_z}{\partial z^2} = 2\pi n_1 j \left(\frac{-3}{r_1^2}\right) \{\cos \theta_A (\sin \theta_A)^4 - \cos \theta_B (\sin \theta_B)^4 - \cos \theta_C (\sin \theta_C)^4 + \cos \theta_D (\sin \theta_D)^4\} \dots\dots(19).$$

Thus the correcting factor  $1 + Br_2^2/(2A)$  in (12) comes to

$$1 + \frac{3}{8} \left(\frac{r_2}{r_1}\right)^2 \frac{\cos \theta_A (\sin \theta_A)^4 - \cos \theta_B (\sin \theta_B)^4 - \cos \theta_C (\sin \theta_C)^4 + \cos \theta_D (\sin \theta_D)^4}{\cos \theta_A - \cos \theta_B - \cos \theta_C + \cos \theta_D} \dots\dots(20).$$

And on inserting the dimensions given in § 2 this comes to 1.0028; the weight for a given current being larger in this ratio than the first approximation indicated.

## DISCUSSION

Dr E. H. RAYNER: I should like to draw attention to the utility of the electromagnetic arrangement of the coils used in the Kelvin Balance for the purpose of physical measurements generally. In the absolute attracted disc voltmeter of the Kelvin type, developed by Palm and made by Hartmann and Braun, in which the active disc is about 2 or 3 cm. in diameter and the working distance about 0.5 cm., the attractive force is balanced by the force produced by current in coils of the type used in the Kelvin Balance; for this purpose a small continuous current is derived from a battery of a few volts and adjusted by means of variable resistance. The main object of this voltmeter is to enable voltages of a few hundred kilovolts to be measured, the whole system being immersed in compressed nitrogen. The observations are made through a telescope and the adjustment is effected by means of a long insulating handle. An accuracy of the order of 1 per cent. is claimed. The forces due to convection currents have been found to be one of the limitations of the accuracy of this type of instrument. The double arrangement, with coils suspended from each arm of the balance, is necessary as thereby the forces are largely balanced.

THE PRESIDENT: I should like to ask what percentage accuracy can be easily ensured in weighing a current of about an ampere, and whether the apparatus shown can be recommended for the calibration of ammeters and the like in circumstances where substandards are not available.

Dr L. F. RICHARDSON: (In reply to the President). The accuracy at one ampere is about 0.5 per cent. We have used this balance for standardizing an ammeter. Our main intention however has been to provide an instructional absolute instrument to serve the same purpose for Final students as does the tangent galvanometer for Intermediate students.

(In reply to Dr Rayner's remarks about convection.) We do always eliminate the greater part of the force due to convection by reversal of the current in the inner coil relative to its sense in the outer coil. It is only the irregular turbulent variations in the convection-currents that limit the accuracy. The double arrangement, with coils suspended to each arm of the balance, would double the electromagnetic force, but would be likely also to increase the "standard deviation" of the turbulent force in the ratio  $\sqrt{2}$ ; so that the fractional uncertainty would be reduced only in the ratio  $\frac{1}{2}\sqrt{2}$ , which is not important in an instructional instrument. But doubling the coils would save time otherwise spent on reversals.

# SOME NOTES ON WIRELESS METHODS OF INVESTIGATING THE ELECTRICAL STRUCTURE OF THE UPPER ATMOSPHERE. I\*

By E. V. APPLETON, F.R.S.

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**ABSTRACT.** Various direct wireless methods of measuring the "effective" height of the atmospheric ionized layer are discussed and compared. For a layer of horizontal stratification, and under conditions for which the influence of the earth's magnetic field may be neglected, the general equivalence of the quantities measured by the various methods is demonstrated. The effective height in such cases is shown to be greater than the maximum height reached by the atmospheric ray. Proposals for using these methods to obtain information concerning the gradient of ionization in the layer are put forward.

## § 1. INTRODUCTION.

WITHIN the last few years various direct wireless methods have been proposed for determining the "effective" height of the ionized layer in the upper atmosphere. There is a somewhat wide divergence in the experimental values obtained by these methods so that it is pertinent to inquire what significance should be attached to the term "effective" in the various cases and also to ascertain whether any agreement is to be expected if the experiments are conducted under similar conditions of wave-length, location, etc. It is easily seen that, if we are dealing with cases of true reflection at a very sharply bounded and highly conducting layer, the track of the atmospheric waves being entirely in unionized air, all the methods should give the same result. If, however, the waves are returned to the ground by the process of "ionic refraction"† in a dispersive medium a more detailed examination is necessary before any corresponding statement can be made. The various methods are therefore discussed in greater detail below.

## § 2 (a). WAVE-LENGTH CHANGE METHOD.

This method was proposed by Appleton and Barnett and used on transmissions from the Bournemouth B.B.C. station received at Oxford‡. More recently it has been developed at the Peterborough Radio Research Station of the Department of Scientific and Industrial Research.

To illustrate the principles of this method let us consider a sending station at *A* (see Fig. 1) sending to a receiving station at *E*. In the ideal case of an ionized layer

\* Paper read at the Brussels meeting of the Union Radio Scientifique Internationale, Sept. 13, 1928.

† *Vide Eccles, Proc. R. S. A., 87, 79 (1912) and Larmor, Phil. Mag. (6), 48, 1025 (1924).*

‡ *Nature*, March 7, 1925.



of horizontal stratification two sets of waves are received at  $E$ , the ground waves travelling direct along  $AE$  and the atmospheric waves travelling via  $ABCHE$ . Let the optical path difference between these two tracks be  $D$ , where  $D$  is, in general, a function of the wave-length of the radiation. We then have

$$n = \frac{D}{\lambda} \quad \dots\dots(1),$$

where  $n$  is the number of wave-lengths the atmospheric waves are behind the ground waves at the point  $E$  and  $\lambda$  is the wave-length in *vacuo*. We have, further,

$$D = \int_{ACE} \mu ds - AE \quad \dots\dots(2),$$

where  $\mu$  is the refractive index at any point and  $ds$  is an element of length of the atmospheric ray path\*.

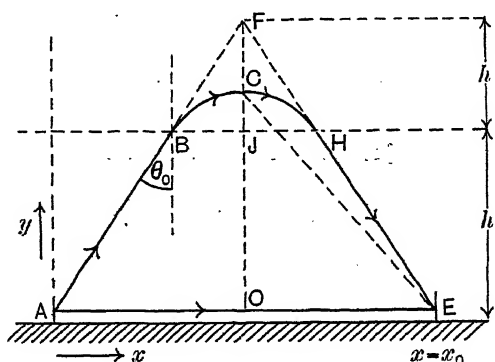


Fig. 1.

The experimental procedure in the wave-length change method consists in measuring the variation in  $n$  (as shown by the signal current maxima and minima experienced at  $E$ ) when  $\lambda$  is continuously varied through a small range. From (1) the variation in  $n$  is given by

$$\delta n = -\frac{D}{\lambda^2} \delta \lambda + \frac{1}{\lambda} \delta D \quad \dots\dots(3).$$

It has been usual to neglect the variation of  $D$  in (3) and consider  $\lambda^2 \frac{\delta n}{\delta \lambda}$  as the "equivalent path difference" between atmospheric and ground ray paths from which, by simple triangulation, the "equivalent height" of the deviating layer was obtained. The justification of the use of the term "equivalent height" in this connection will be seen in what follows.

It is shown in Appendix 1 that for a variation in optical path due to a finite change of wave-length such as we are considering, we have

$$\delta D = \delta \int_{ACE} \mu ds = \int_{ACE} \frac{\partial \mu}{\partial \lambda} ds \delta \lambda \quad \dots\dots(4),$$

\* The possibility of the dispersion of the ground waves is discussed below.

so that, combining with (2) and (3) we have

$$-\lambda^2 \frac{\delta n}{\delta \lambda} = \int_{ACE} \mu ds - \lambda \int_{ACE} \frac{\partial \mu}{\partial \lambda} ds - AE \quad \dots\dots(5).$$

But, from the usual relation between group velocity  $U$ , refractive index and wave-length we have, as shown in Appendix II,

$$c \int \frac{ds}{U} = \int \mu ds - \lambda \int \frac{\partial \mu}{\partial \lambda} ds \quad \dots\dots(6),$$

where  $c$  is the velocity of radiation in free space, so that from (5) and (6) we have

$$\lambda^2 \frac{\delta n}{\delta \lambda} = c \int_{ACE} \frac{ds}{U} - AE \quad \dots\dots(7),$$

where the negative sign of the experimentally determined quantity  $\lambda^2 \frac{\delta n}{\delta \lambda}$  has been omitted since  $\delta n$  is negative for an increase of wave-length. We thus see that the "equivalent path difference" is equal to the product of the velocity in free space multiplied by the temporal retardation of a signal traversing the atmospheric path with its appropriate group velocity compared with a signal traversing the ground path. This is quite a different quantity from the actual path difference obtained from (3) by neglecting  $\delta D$  for which approximation we should write, using (2),

$$\lambda^2 \frac{\delta n}{\delta \lambda} = \int_{ACE} \mu ds - AE \quad \dots\dots(7 a).$$

In the case in which the influence of the earth's magnetic field may be neglected (e.g. with short waves) it is easy to show that  $U = c\mu$  so that, for such conditions the optical path of the atmospheric ray would be  $\int \mu ds$  while the equivalent path would be  $\int \frac{ds}{\mu}$ .

It should be mentioned here that, strictly speaking, we should also write

$$\text{Ground Path} = \int_{AOE} \mu ds \quad \dots\dots(8),$$

so that for a variation in wave-length

$$\delta (\text{Ground Path}) = \int_{AOE} \frac{\partial \mu}{\partial \lambda} ds \delta \lambda \quad \dots\dots(9),$$

leading ultimately to the general result

$$\lambda^2 \frac{\delta n}{\delta \lambda} = c \int_{ACE} \frac{ds}{U} - c \int_{AOE} \frac{ds}{U'} \quad \dots\dots(10),$$

where  $U'$  is the group velocity of the waves along the ground. It seems quite possible that  $U'$  may differ appreciably from  $c$  when very short waves are used.

## § 2 (b). ANGLE OF INCIDENCE METHOD.

This method was proposed by Appleton and Barnett\* and used at Cambridge to determine the angle of incidence of down-coming waves emitted by the London B.B.C. transmitter. It has also been used by Smith-Rose and Barfield† in a comprehensive study of down-coming waves received from various stations. When the angle of incidence is known the "effective height" of the layer deviating the waves is found by simple triangulation. This quantity would correspond to  $FO$  in Fig. 1.

In the general case of magneto-ionic refraction in which the influence of the earth's magnetism is taken into account it is difficult to interpret these experiments much further. If, however, we neglect this influence and also assume that the layer is horizontally stratified a correlation with the wave-length change method may be effected. Since, in such a case, the experimentally determined angle of incidence  $\theta_0$  at the ground is also equal to the angle of incidence at the layer we may write

$$\mu \sin \theta = \sin \theta_0 \quad \text{.....(11),}$$

where  $\theta$  is the angle the atmospheric ray makes with the vertical at any point at which the index of refraction of the medium is  $\mu$ . Also, as before, we have

$$U = c\mu \quad \text{.....(12).}$$

Thus, since  $dx = ds \sin \theta$  for the atmospheric ray, we have, using (11) and (12)

$$c \int \frac{ds}{U} = \int \frac{ds}{\mu} = \int \frac{dx}{\sin \theta_0} = (AF + FE) \quad \text{.....(13).}$$

The quantity  $c \int \frac{ds}{U}$ , as Breit and Tuve‡ first pointed out, is therefore equal to the fictitious path  $AFE$  (see Fig. 1). We thus see that, in the case of short waves, the equivalent path of the atmospheric waves measured by the wave-length change method is equal to the effective path obtained by simple triangulation using the angle of incidence of the waves as measured at the ground. Thus both methods (a) and (b) give the height  $FO$  which is greater than the true height  $CO$  (see Fig. 1).

## § 2 (c). GROUP-RETARDATION METHOD.

This method was first proposed and used by Breit and Tuve§ who used a transmitter sending out short pulses of radio-frequency energy and measured the time interval  $\Delta t$  between the arrival of the signal pulses received via the ground and via the atmosphere.

For such a case, using again Fig. 1 we may write, simply,

$$\Delta t = \int_{ACE} \frac{ds}{U} - \int_{AOE} \frac{ds}{U'} \quad \text{.....(14),}$$

from which the general equivalence of what is measured in the wave-length change method and in the group retardation method is at once apparent.

\* *Electrician*, April 3, 1925, p. 398 and *Proc. R. S. A*, 109, 621 (1925).

† *Proc. R. S. A*, 110, 580 (1926) and 116, 682 (1927).

‡ *Physical Review*, 28, No. 3, 571 (1926).

§ *Loc. cit.*

It has, however, been pointed out to me by Mr J. A. Ratcliffe that (14) applied to the group-retardation method requires qualification, since the component frequencies of the group do not follow the same path. The problem is therefore a little more complicated than that contemplated in the ordinary discussions of group velocity in which the frequency components (usually two) of the group travel along the same (usually straight) path. The following justification of the applicability of (14) is therefore offered. The case of a particularly simple type of group transmission which has not yet been tried in practice is first examined. The discussion of the actual type of group transmission used by Breit and Tuve then follows.

Let us consider the simplest case of the transmission of a group of waves and imagine two sets of waves, the frequencies of which differ only slightly, emitted by a sending station. If the angular frequencies of the waves are  $p - \delta p$  and  $p + \delta p$  beats of frequency  $\frac{\delta p}{\pi}$  will be produced when the waves travel in unionized air along the same track. For both sets of waves to arrive at the same receiving station (e.g.  $E$  in Fig. 1) they must set out from the sending station along slightly different directions because of the dispersion in the ionized layer. To allow for the difference in frequency and for the difference in the optical paths of the two components we say that the received signal amplitude is proportional to

$$\cos(p - \delta p) \left( t - \frac{P - \delta P}{c} \right) + \cos(p + \delta p) \left( t - \frac{P + \delta P}{c} \right) \dots\dots(15),$$

or to 
$$2 \cos p \left( t - \frac{P}{c} \right) \cos \left( \frac{\delta p P}{c} + \frac{p \delta P}{c} - t \delta p \right) \dots\dots(16),$$

where  $P$  is the optical path of the atmospheric ray for angular frequency  $p$ . The expression for the received signal amplitude represents a high frequency oscillation of slowly varying amplitude. The particular maximum amplitude emitted by the sending station when  $t$  and  $P$  are zero is reproduced again at the receiver after a time  $t$  given by

$$\frac{\delta p P}{c} + \frac{p \delta P}{c} - t \delta p = 0,$$

or by 
$$ct = \int \mu ds + p \frac{\delta}{\delta p} \int \mu ds \dots\dots(17)$$

$$= \int \mu ds - \lambda \frac{\delta}{\delta \lambda} \int \mu ds \dots\dots(18).$$

Now from Appendix I we have

$$\int \mu ds = \int \frac{\partial \mu}{\partial \lambda} ds.$$

Thus (18) becomes 
$$ct = \int \mu ds - \lambda \int \frac{\partial \mu}{\partial \lambda} ds \dots\dots(19)$$

$$= c \int \frac{ds}{U} \dots\dots(20).$$

We thus see that a particular beat maximum emitted by the sending station is produced again at the receiving station after a time  $\int \frac{ds}{U}$  where  $U$  is the group

velocity for the mean frequency. The use of (14) is therefore justified even though the two component frequencies have followed slightly different tracks.

To measure the group retardation in such an experiment as has been suggested above, the down-coming waves could be received on a suppressed ground ray system and the high frequency oscillations produced rectified, thus transforming the beats into combination tones. The phase of the combination tone received via the atmosphere could be compared with that of the combination tone received via the ground waves and, from a knowledge of the beat frequency, the retardation found.

An imaginary experiment shows even more closely the essential equivalence of the wave-length change method and the particular type of group retardation method described immediately above. Let us suppose that one of the emitted wave-lengths is maintained constant and the other made gradually different so that the beat frequency increases from zero. The phase difference between the beat amplitudes received via the atmosphere and via the ground will gradually increase. Let us now suppose that when the wave-lengths differ by  $\delta\lambda$  the phase difference is  $\phi$  where  $\phi$  is  $2\pi n'$ . The group retardation  $\Delta t$  is then evidently  $n't'$ , where  $t'$  is the time of one beat\*. But  $t'$  is equal to  $\frac{\lambda^2}{c\delta\lambda}$ , so that, using again Fig. 1, we have

$$\Delta t = \int_{ACE} \frac{ds}{U} - \int_{AOE} \frac{ds}{U'} = n' \left( \frac{\lambda^2}{c\delta\lambda} \right) \quad \dots\dots(21).$$

But if the two wave-lengths emitted by the sending station had been the initial and final wave-lengths during a wave-length change experiment we should have from (10)

$$\lambda^2 \frac{\delta n}{\delta \lambda} : \int_{ACE} \frac{ds}{U} - \int_{AOE} \frac{ds}{U'} \quad \dots\dots(22),$$

so that

$$n' = \delta n.$$

Thus the number of "fringes" measured in the wave-length change method is equal to the number of beats the atmospheric ray is behind the ground ray when the beats are produced by the simultaneous emission of the initial and final wave-lengths used.

The extension to the case of pulses of radio-frequency waves as actually used by Breit and Tuve follows on similar lines. Let us suppose that the group may be represented by the sum of a large number of sinusoidal vibrations the frequencies of which differ only slightly from  $p/2\pi$ . The disturbance arriving at the receiving station may then be represented by

$$\Sigma a \cos(p + \delta p) \left( t - \frac{P + \delta P}{c} \right),$$

which is equal to

$$\begin{aligned} & \cos p \left( t - \frac{P}{c} \right) \Sigma a \cos \left( t\delta p - \delta p \frac{P}{c} - p \frac{\delta P}{c} \right) \\ & - \sin p \left( t - \frac{P}{c} \right) \Sigma a \sin \left( t\delta p - \delta p \frac{P}{c} - p \frac{\delta P}{c} \right). \end{aligned}$$

\* In other words,  $n'$  is the time interval between the beats as received via the atmosphere and via the ground, expressed in terms of a beat period as unit of time.

We thus get the reproduction of the original wave-form (i.e. the group is received) at the receiver when

$$t \delta p - \delta p \frac{P}{c} - p \frac{\delta P}{c} = 0,$$

or when

$$t = \frac{1}{c} \left( \int \mu ds + p \frac{\delta}{\delta p} \int \mu ds \right) \quad \dots\dots(23).$$

But (23) is identical with (17) which was shown to lead to

$$t = \int \frac{ds}{U} \quad \dots\dots(24).$$

In this case  $t$  is the time of transmission of the group through the atmosphere and  $U$  the group velocity of the mean frequency. In the actual experiment of Breit and Tuve the use of (14) may therefore be justified even when the different components of the group follow different tracks in the upper atmosphere.

It will be seen that, for the measurement of the group-retardation, it is not necessary to send out "chopped"\* signals like those used by Breit and Tuve. A sinusoidally-modulated wave would suffice for receiving stations at which the ground waves are strong. In the case of short waves and fairly long transmission distances the ground waves would be strongly absorbed and thus of negligible strength at the receiver. In such cases the modulation signal or the "chopped" signals of Breit and Tuve could be transmitted simultaneously along the ground by a much longer wireless wave-length or possibly by telephone.

Summarising the results of this section we may say that:

(1) The wave-length change method and the group-retardation method measure the same quantity (i.e.  $c \int \frac{ds}{U}$  for the atmospheric waves).

(2) In cases for which the effect of the earth's magnetic field is negligible and the layer is horizontally stratified, the above-mentioned methods, together with the angle of incidence method, give us the equivalent height  $FO$  in Fig. 1. The equivalent height is greater than the actual maximum height reached by the atmospheric waves.

### §3. SOME SPECIAL IONIZATION GRADIENTS

It is instructive to consider some of the questions discussed above for some particular types of ionization gradients in the layer.

Let us suppose (see Fig. 2 in which the lettering is the same as in Fig. 1) that a ray enters the layer at  $B$ , and that the gradual deviation of it is brought about by the gradual reduction of the refractive index (due to the increasing ionization) experienced as it penetrates the layer. Consider any point  $P$  on the path of the ray and let the tangent to the path at that point make an angle  $\theta$  with the vertical (i.e. with the  $y$  axis in the figure). We then have, as before,

$$\mu \sin \theta = \mu_0 \sin \theta_0 = \sin \theta_0 \quad \dots\dots(25),$$

\* A simple method of obtaining these short trains of oscillations is to use a transmitter with a high grid leak the circuit being similar to that used for producing the unidirectional cathode-ray oscillograph time base. *Vide Proc. R. S. A.*, 111, 672 (1926).

where  $\mu$  is the refractive index at the point  $P$  and  $\mu_0 (= 1)$  is the refractive index of the unionized air.  $\theta_0$  is the angle of incidence at the layer. The refractive index  $\mu$  is considered as being independent of  $x$  and dependent only on  $y$  and the wave-length.

Since 
$$\tan \theta = \frac{dx}{dy},$$

and

$$ds = \sqrt{1 + \tan^2 \theta} dy,$$

the optical path in the medium is given by

$$\begin{aligned} \int \mu ds &= 2 \int_0^{y_0} \mu \sqrt{1 + \left(\frac{dx}{dy}\right)^2} dy \\ &= 2 \int_0^{y_0} \frac{\mu^2}{\sqrt{\mu^2 - \sin^2 \theta_0}} dy \end{aligned} \quad \dots\dots(26)$$

where  $\mu = f(y, \lambda)$  and  $\sin \theta_0 = f(y_0, \lambda)$ .

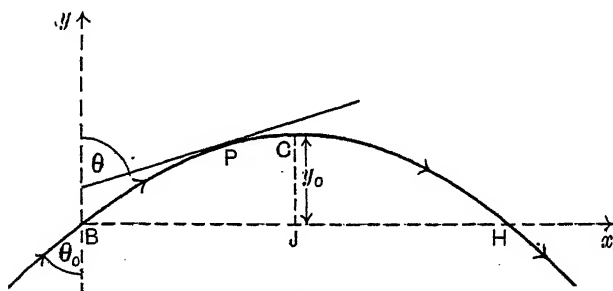


Fig. 2.

Correspondingly we have for the "equivalent" path

$$\int \frac{ds}{\mu} = 2 \int_0^{y_0} \frac{dy}{\sqrt{\mu^2 - \sin^2 \theta_0}} \quad \dots\dots(27).$$

The above expressions have been derived on the assumption that  $\mu$  is a single-valued function of position for constant wave-length and so the argument only applies to the case in which the influence of the earth's magnetic field is negligible. We therefore consider the case as applying to the propagation of short waves. For this reason we may take simple types of variation of the refractive index such as

$$\mu^2 = 1 - \alpha y \quad \dots\dots \text{Case } (\alpha),$$

and

$$\mu^2 = 1 - \beta y^2 \quad \dots\dots \text{Case } (\beta).$$

Case ( $\alpha$ ) corresponds to a gradient in which the ionization varies directly with the height above the lower boundary of the layer, while Case ( $\beta$ ) corresponds to ionization varying as the square of the height. By substituting for  $\mu^2$  in (25) and (26) and integrating it is possible to arrive at the following results for the two cases.

Case ( $\alpha$ ).  $\mu^2 = 1 - \alpha y$ :

$$\left. \begin{aligned} \text{Optical path in the layer} &= \int \mu ds = \frac{4}{\alpha} \cos \theta_0 - \frac{8}{3\alpha} \cos^3 \theta_0 \\ \text{Equivalent path in the layer} &= \int \frac{ds}{\mu} = \frac{4}{\alpha} \cos \theta_0 \\ \text{Horizontal distance in the layer (BH in figure)} &= \frac{4}{\alpha} \sin \theta_0 \cdot \cos \theta_0 \\ \text{Maximum height in the layer (CJ in figure)} &= \frac{\cos^2 \theta_0}{\alpha} \end{aligned} \right\} \dots\dots(28).$$

Case ( $\beta$ ).  $\mu^2 = 1 - \beta y^2$ :

$$\left. \begin{aligned} \text{Optical path in the layer} &= \int \mu ds = \frac{\pi}{2\sqrt{\beta}} (1 + \sin^2 \theta_0) \\ \text{Equivalent path in the layer} &= \int \frac{ds}{\mu} = \frac{\pi}{\sqrt{\beta}} \\ \text{Horizontal distance in the layer} &= \frac{\pi \sin \theta_0}{\sqrt{\beta}} \\ \text{Maximum height in the layer} &= \frac{\cos \theta_0}{\sqrt{\beta}} \end{aligned} \right\} \dots\dots(29).$$

Now in attempting to verify for the above examples that the equivalent path  $\int \frac{ds}{\mu}$ , which is the quantity measured in the group-retardation method, is the same as the quantity  $\int \mu ds - \lambda \frac{\delta}{\delta \lambda} \int \mu ds$  measured in the wave-length change method, we have to consider the problem as a whole and recognise that both the angle of incidence at the layer and the track in and out of the layer all vary when we vary the wave-length. Let us therefore consider the complete problem of a layer situated at a distance  $h$  above the ground (see Fig. 1) and take the case of transmission between two points a distance  $d$  (i.e.  $AE$  in Fig. 1) apart. For stationary conditions of wave-length we can write in the two cases:

Case ( $\alpha$ ):

$$\left. \begin{aligned} \text{Total optical path of atmospheric ray} &= \int \mu ds = \frac{2h}{\cos \theta_0} + \frac{4}{\alpha} \cos \theta_0 - \frac{8}{3\alpha} \cos^3 \theta_0 \\ \text{Total equivalent path of atmospheric ray} &= \int \frac{ds}{\mu} = \frac{2h}{\cos \theta_0} + \frac{4}{\alpha} \cos \theta_0 \\ \text{Path of ground ray} &= d = 2h \tan \theta_0 + \frac{2}{\alpha} \sin 2\theta_0 \end{aligned} \right\} \dots\dots(30).$$

Case ( $\beta$ ):

$$\left. \begin{aligned} \text{Total optical path of atmospheric ray} &= \int \mu ds = \frac{2h}{\cos \theta_0} + \frac{\pi}{2\sqrt{\beta}} (1 + \sin^2 \theta_0) \\ \text{Total equivalent path of atmospheric ray} &= \int \frac{ds}{\mu} = \frac{2h}{\cos \theta_0} + \frac{\pi}{\sqrt{\beta}} \\ \text{Path of ground ray} &= d = 2h \tan \theta_0 + \frac{\pi \sin \theta_0}{\sqrt{\beta}} \end{aligned} \right\} \dots\dots(31).$$



Now the recognition of the essential equivalence of the wave-length change method and the group-retardation method was based on the proof that, for such cases as we are considering  $\int \mu ds - \lambda \frac{\delta}{\delta \lambda} \int \mu ds$  was equal to the equivalent path  $\int \frac{ds}{\mu}$ . In attempting to demonstrate this for these particular cases we note that, in finding the value of the expression  $\frac{\delta}{\delta \lambda} \int \mu ds$ , we require to know both  $\frac{\partial \alpha}{\partial \lambda}$  (or  $\frac{\partial \beta}{\partial \lambda}$ ) and  $\frac{\partial \theta_0}{\partial \lambda}$ , for the expression for  $\int \mu ds$  involves both these quantities. Now in an ionized medium in which the frequency of the electronic collisions with the gas molecules is small, we may write

$$\mu^2 = 1 - A\lambda^2 \quad \dots\dots(32),$$

where  $A$  is a quantity\* which is proportional to the ionization. Thus for our two cases we have

$$\text{Case } (\alpha) \quad \mu^2 = 1 - \alpha y = 1 - B\lambda^2 y,$$

$$\text{Case } (\beta) \quad \mu^2 = 1 - \beta y^2 = 1 - C\lambda^2 y^2,$$

where  $B$  and  $C$  are constants. From these expressions  $\frac{\partial \alpha}{\partial \lambda}$  and  $\frac{\partial \beta}{\partial \lambda}$  may be calculated.

Also, from the expressions for the total path of the ground ray in each case we can find  $\frac{\partial \theta_0}{\partial \lambda}$  after making the substitution for  $\frac{\partial \alpha}{\partial \lambda}$  or  $\frac{\partial \beta}{\partial \lambda}$  as the case may be. In this way we arrive at the value of  $\int \mu ds - \lambda \frac{\delta}{\delta \lambda} \int \mu ds$  for the total atmospheric paths in the two cases. These are found to be

$$\text{Case } (\alpha) \quad \int \mu ds - \lambda \frac{\delta}{\delta \lambda} \int \mu ds = \frac{2h}{\cos \theta_0} + \frac{4}{\alpha} \cos \theta_0 \quad \dots\dots(33),$$

$$\text{Case } (\beta) \quad \int \mu ds - \lambda \frac{\delta}{\delta \lambda} \int \mu ds = \frac{2h}{\cos \theta_0} + \frac{\pi}{\sqrt{\beta}} \quad \dots\dots(34).$$

But from (30) and (31) we see that these expressions are exactly those for the equivalent paths. We therefore have verified the statement that in the wave-length change method we measure the equivalent path  $\int \frac{ds}{\mu}$  and not the optical path  $\int \mu ds$ .

From the point of view of deducing information concerning  $\alpha$  and  $\beta$  from experimental determinations of  $c \Delta t$  or  $\lambda^2 \frac{\delta n}{\delta \lambda}$  we note that the relevant equations are as follows:

$$\text{Case } (\alpha) \quad c \Delta t = \lambda^2 \frac{\delta n}{\delta \lambda} = \frac{2h}{\cos \theta_0} + \frac{4}{\alpha} \cos \theta_0 - d \quad \dots\dots(35).$$

$$\text{Case } (\beta) \quad c \Delta t = \lambda^2 \frac{\delta n}{\delta \lambda} = \frac{2h}{\cos \theta_0} + \frac{\pi}{\sqrt{\beta}} - d \quad \dots\dots(36).$$

\*  $A$  is actually equal to  $\frac{Ne^2}{\pi mc^2}$  where  $N$  is the number of electrons, of charge  $e$  and mass  $m$ , per c.c.

## § 4. METHODS OF INVESTIGATING THE IONIZATION GRADIENT

We have seen that for short waves any one of the three methods discussed above will enable us to find the value of  $\int \frac{ds}{\mu}$  for the atmospheric ray. This quantity is equal to the length  $AFE$  in Fig. 3, from which, knowing  $d$ , we may find  $\sin \theta_0$ , which is equal to the refractive index at the point  $C$ . Now since, for short waves, we have

$$\mu^2 = 1 - \frac{4\pi Ne^2}{mp^2} \quad \dots\dots(37),$$

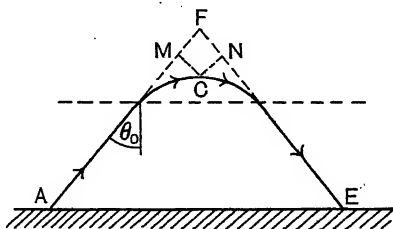


Fig. 3.

a knowledge of the refractive index enables us to calculate the electron concentration  $N$  at the point  $C$ . If we could measure the actual height of point  $C$  in some other way we should be able to specify the ionization at a particular height.

Let  $CM$  and  $CN$  (in Fig. 3) be perpendiculars from  $C$  on  $AF$  and  $FE$  respectively. Now Pedersen has shown\* that the optical path  $\int \mu ds$  of the atmospheric ray, when  $\theta_0 > 30^\circ$ , is approximately (actually slightly smaller than)  $AM + NE$ . If, therefore, it were possible to determine both  $\int \frac{ds}{\mu}$  and  $\int \mu ds$  for the atmospheric ray we should be able to find both the ionization at and height of point  $C$ . The equivalent path would fix for us the position of  $F$  and enable us to calculate the ionization at  $C$ , while the optical path would fix the positions of  $M$  and  $N$  from which the position of  $C$  could be found. To a method of estimating the optical path of the atmospheric ray we now turn.

It will be found convenient to re-write (1) in terms of the frequency  $f$  instead of the wave-length  $\lambda$ . Thus

$$n = \frac{fD}{c}$$

and

$$\frac{dn}{df} = \frac{D}{c} + \frac{f}{c} \frac{dD}{df} \quad \dots\dots(38).$$

Now it is possible to carry out experiments in which  $\frac{dn}{df}$  is measured for a large number of frequencies at about the same time and under the same conditions of transmission distance, etc. This quantity would, in general, be a function of the frequency and may be written  $\phi(f)$ . Thus (38) becomes

$$\frac{dD}{df} + \frac{D}{f} = \frac{c}{f} \phi(f) \quad \dots\dots(39),$$

\* *The Propagation of Radio Waves*, Copenhagen, 1927, p. 176.

the solution of which is given by

$$Df = c \int \phi(f) df + \text{const.} \quad \dots\dots(40).$$

We thus see that, even if  $\phi(f)$  is known for a considerable range of frequencies, we cannot find  $D$  exactly for any particular frequency since the constant is unknown. If, however, after having obtained values of  $\phi(f)$  for as low frequencies as we can in practice, we draw the curve showing the relation between  $\phi(f)$  and  $f$  and extrapolate it to the limit of zero frequency we can get over this difficulty and write

$$D_0 f_0 = c \int_0^{f_0} \phi(f) df \quad \dots\dots(41),$$

where  $D_0$  is the optical path difference for a particular frequency  $f_0$ . The optical path of the atmospheric ray for the very high frequencies could then be found and the ionization at certain particular heights determined by the method outlined above.

It should be noted that the measurements of  $\frac{dn}{df}$  would have to be made at a considerable distance from the transmitter to fulfil the conditions under which the relation of Pedersen holds, and it is most probable that, as the frequency is increased to the values for which the influence of the earth's magnetic field is negligible, the strength of the ground waves at the receiving station would be too small to detect. In such cases the suggestion made above of using at the same time a long wave-length to send out the modulation (e.g. pulses of Breit and Tuve) might be useful.

The method described above deals with measurements made at one receiving station with different mean frequencies. It is, however, possible that information of similar character might be obtained by making simultaneous observations on the same mean frequency at different distances as the following considerations show.

We have seen that any one of the three direct methods considered will enable us to find the equivalent height  $OF$  (i.e.  $h + h'$  in Fig. 1). Considering again the cases of special types of ionization gradients we find from (35)

$$\lambda^2 \frac{\delta n}{\delta \lambda} + d = \frac{2(h + h')}{\cos \theta_0} = \frac{2h}{\cos \theta_0} + \frac{4 \cos \theta_0}{\alpha},$$

$$\text{or} \quad h + h' = h + \frac{2}{\alpha} \cos^2 \theta_0 \quad \dots\dots(42),$$

$$\text{and similarly from (36)} \quad h + h' = h + \frac{\pi \cos \theta_0}{2\sqrt{\beta}} \quad \dots\dots(43).$$

We thus see that, for a case of ionization varying directly with the height, the equivalent height should vary linearly with  $\cos^2 \theta_0$  for observations made at various distances, whereas for ionization varying as the square of the height the equivalent height should vary linearly with  $\cos \theta_0$ . Corresponding equations for other types of gradient could be found and by comparing the equivalent heights at different distances we should be able to ascertain which type of gradient gives the closest approximation. When this decision has been made the observations from any two stations would enable us to find both  $h$  and  $\alpha$  (or  $\beta$ ) from which the ionization at

definite heights could be stated. Additional evidence could be obtained by making the experiments with different wave-lengths since  $\alpha$  (or  $\beta$ ) depends on the wave-length. For example, once the type of gradient had been determined, it would also be possible to find  $h$  and  $\alpha$  (or  $\beta$ ) from observations made at any one station on two different wave-lengths. The results could therefore be checked.

In a later communication I hope to deal with the more practical aspects of some of the theoretical points discussed in the present paper. These problems have arisen in connection with investigations carried out for the Radio Research Board of the Department of Scientific and Industrial Research.

# APPENDIX I

## *To find the variation in the optical path of the atmospheric ray*

Consider Fig. 1 in which the track of the atmospheric ray *ABCHE* begins at the origin *A* and finishes at *E* ( $x_0, 0$ ). We have

$$\int \mu ds = \int_0^{x_0} \mu \frac{ds}{dx} dx \quad \dots\dots(1').$$

Now if the refractive index is (as in the most general case of the magneto-ionic theory) a function of position, ray-direction and wave-length we write

$$\mu = f(x, y, z, \lambda, y', z') \quad \dots\dots(2').$$

Thus

$$\begin{aligned} \delta \int \mu ds &= \delta \int_0^{x_0} \mu \frac{ds}{dx} dx \\ &= \int_0^{x_0} \delta \mu \frac{ds}{dx} dx + \mu \delta \left( \frac{ds}{dx} \right) dx \\ &= \int_0^{x_0} \left\{ \frac{\partial \mu}{\partial y} \delta y + \frac{\partial \mu}{\partial z} \delta z - \frac{d}{dx} \left( \frac{\partial \mu}{\partial y'} \right) \delta y - \frac{d}{dx} \left( \frac{\partial \mu}{\partial z'} \right) \delta z + \frac{\partial \mu}{\partial \lambda} \delta \lambda \right\} \frac{ds}{dx} dx \\ &\quad + \int_0^{x_0} \mu \delta \left( \frac{ds}{dx} \right) dx \quad \dots\dots(3'). \end{aligned}$$

But by the principle of least time, as interpreted by Hamilton, the terms on the right-hand side representing path variations vanish, leaving only the term involving the wave-length variation. Thus

$$\begin{aligned} \delta \int \mu ds &= \int_0^{x_0} \frac{\partial \mu}{\partial \lambda} \delta \lambda \frac{ds}{dx} dx \\ &= \int \frac{\partial \mu}{\partial \lambda} ds \delta \lambda \quad \dots\dots(4'). \end{aligned}$$

## APPENDIX II

*The relation between phase and group velocities*

The relation between group velocity  $U$  and phase velocity  $V$  is given by

$$\frac{1}{U} = \frac{\partial}{\partial f} \left( \frac{f}{V} \right) \quad \dots\dots(1'')$$

where  $f$  is the frequency of the waves. But  $V$  is equal to  $\frac{c}{\mu}$  so that this becomes

$$\begin{aligned} \frac{1}{U} &= \frac{1}{c} \frac{\partial}{\partial f} (f\mu) \\ &= \frac{1}{c} \left( \mu + f \frac{\partial \mu}{\partial f} \right) \\ &= \frac{1}{c} \left( \mu - \lambda \frac{\partial \mu}{\partial \lambda} \right) \quad \dots\dots(2''). \end{aligned}$$

Thus for any particular path we have

$$c \int \frac{ds}{U} = \int \mu ds - \lambda \int \frac{\partial \mu}{\partial \lambda} ds \quad \dots\dots(3'').$$

This equation is to be compared with

$$\lambda^2 \frac{\delta n}{\delta \lambda} + AE = \int \mu ds - \lambda \frac{\delta}{\delta \lambda} \int \mu ds \quad \dots\dots(4''),$$

which may be derived from (2) and (3).

In conclusion I wish to express my particular indebtedness to my collaborator Mr J. A. Ratcliffe, who first raised the question of the essential equivalence of the quantities measured in the wave-length change method and in the method of Breit and Tuve by pointing out to me the close similarity between equations (3'') and (4''), which are the representative relations for the two methods. To Mr S. Goldstein I am also greatly indebted for advice on certain mathematical points.

## DISCUSSION

Dr J. HOLLINGWORTH: The few words I have to say are concerned more with the practical than with the theoretical side of this paper. In the diagrams a fairly small angle of incidence ( $\theta_0$ ) is generally shown corresponding to short distances of transmission, under which conditions the experiments have, I believe, been made. It remains uncertain, however, how far this method would serve for determining whether the effective height is independent of the angle of incidence for larger values of the latter. On page 53 it is specified that  $\theta_0 > 30^\circ$  and personally I should be inclined to put this figure definitely higher. My own experience (which, it is true, is derived from a study of very long waves) suggests strongly that for longer distances of transmission the path is definitely of a "flat-topped" form rather than triangular, though decisive evidence is very difficult to obtain.

Mr T. SMITH: I am induced to speak on Prof. Appleton's paper because his treatment of the subject involves essentially the same considerations as those which enter into optical problems. Optical experience suggests that if we are measuring the directions in which waves travel, or the statistical distribution of their energy in space, we shall be concerned with  $\int \frac{ds}{\mu}$  rather than with the integral  $\int \mu ds$  from which we start. Almost any measurement we like to make will relate to the former rather than to the latter. In fact it is not at all an easy matter to contrive experiments which depend on  $\int \mu ds$ . For instance a signal of any kind must give  $\int \frac{ds}{\mu}$ , for a signal is given by imposing a peculiarity of some kind on a train of waves, that is to say it concerns group velocity, not phase velocity. The fact that group velocity is involved is not always obvious; some of the historic methods employed in measuring the velocity of light afford examples in which the distinction is very subtle. The method of measurement at the receiving end has to be carefully considered before we can be sure that it is the phase velocity which is being obtained. For example, consider directional measurement with a monorhythmic train of waves. If this be carried out by cutting off a portion of the wave front our experiments will give the group, not the phase velocity, for in isolating a part of a wave we have impressed a peculiarity on it, and it is this peculiarity we are measuring. It is therefore fortunate that the quantity we are most often interested in is the one it is simpler to obtain. If in optics we desired to evaluate  $\int \mu ds$  we should fall back upon an interference method, preferably one in which we obtained "white light fringes." Perhaps a corresponding method, in which the time taken by an interfering wave to travel between source and receiver can be controlled and adjusted to give steady agreement of phase with the reflected beam for a range of wave-lengths, would be possible in the wireless problem.

Professor Appleton has shown that  $\int \frac{ds}{\mu}$  is related to the length of hypothetical rectilinear paths observed from the ground. We can also relate it to the area enclosed by the wave in its actual path, and the comparison of the two may perhaps give some useful information. Instead of regarding the refracting layers as planes, let us take into account the curvature of the earth: the layers of equal refractive index are then concentric spheres. We may now apply the well-known optical law that the product of the refractive index and the perpendicular to the ray from the centre of the refracting surfaces is constant. Thus  $\mu p = P$ . Now the area of the triangle having the earth's centre as vertex and the element of path  $ds$  as base is  $\frac{1}{2} p ds$ . It follows that

$$\int_A^B \frac{ds}{\mu} = \int_A^B \frac{p ds}{\mu p} = \frac{2\Delta}{P},$$

where  $\Delta$  is the area enclosed between the path  $AB$  and the straight lines  $AG$  and  $BG$  joining  $A$  and  $B$  to  $G$ , the centre of the earth. From the observed height of the point  $F$  in Prof. Appleton's diagram the area of the trapezium  $AFEG$  can

be found. The difference between this and the area  $ABCHEG$  follows, that is to say the area  $BFHC$ . A superior correction  $C'F$  to the height of  $OF$  is obtained by assuming that the path in air consists of three straight portions along  $AF$ , the horizontal through  $C'$  and  $FE$ , respectively, the triangle they enclose having its area equal to that found for  $BFHC$ . A closer approximation can be obtained by assuming that  $BCH$  is a parabolic arc. This leads to the conclusion that the area enclosed by  $AF$ ,  $FE$  and the horizontal through  $C$  should be equal to three-quarters of the area  $BFHC$ .

Prof. A. O. RANKINE: There appears to be an analogy between the phenomena discussed in the paper and seismic phenomena which occur both in natural earthquakes and in surface explosions artificially produced, in which the disturbances travel more rapidly in the deeper strata than in those near the surface. In such cases an appreciable fraction of the total disturbance is found to enter the lower medium at the critical angle, travel along the interface with the velocity corresponding to the lower medium, and re-enter the upper medium again at the critical angle. If the distance between the source of disturbance and the point of observation be great enough, the waves following the above path arrive earlier than those proceeding direct through the upper (or lower-velocity) medium. Since the velocity of wireless waves is enhanced in the Heaviside layer, there would appear to be a close, though inverted, analogy between this seismic phenomenon and the travelling of wireless waves in a "flat-topped" path as described by Dr Hollingworth.

THE PRESIDENT: Prof. Appleton has made the subject his own, especially where short distance propagation is concerned. He started his measurements by assuming as a first approximation that the Heaviside layer is well defined and behaves like a mirror, and he obtained valuable information about the layer on that assumption. Now he is inevitably proceeding to a second step in the approximation by examining into the consequences of assuming a transitional space where ionic refraction occurs. The discussion has brought out that the path of the wave may be considerably different from this second approximation, and may even be a very shallow truncated triangle. However, the common point which appears to emerge is that the deflecting layer is indeed rather sharply defined.

AUTHOR'S reply: Dr Hollingworth's deduction, from his long wave measurements, that  $\theta_0$  may be taken as being larger than  $30^\circ$  is very helpful, in that it indicates that the first of the two methods of finding the ionization gradient might be carried out with some hope of success. So long as  $\theta_0$  is greater than  $30^\circ$ , this method is independent of the path, "flat-topped" or otherwise.

Mr Smith's very interesting result can be used to show how the spherical and plane cases differ. Suppose that, in Fig. 1,  $AOE$  is a curved portion of the earth's surface. Then it may be shown that

$$\int \frac{ds}{\mu} = \frac{AOE}{\sin \theta_0} + \frac{2S}{R \sin \theta_0},$$

where  $S$  is the area included between the atmospheric path and the ground. The

second term on the right-hand side of this equation is the small correction term (cf. equation 13). If it were possible, by very refined measurements, to find  $\int \frac{ds}{\mu}$  and  $\theta_0$  accurately,  $S$  could be found.

The President has raised the important question of the process by which the atmospheric waves are deviated. Although the paper is based on the ionic refraction theory, it may turn out that the ionization gradient is greater than is commonly supposed and that we shall have to replace simple ionic refraction by some process intermediate between such refraction and true reflection. If, in such a case, the boundary of the layer had a certain degree of "roughness," we could possibly explain "skipped distances" as being regions in which only diffusely-reflected radiation is received, the specularly-reflected radiation being received at greater distances. Such an explanation would give the correct relation between the wave-length and the magnitude of the skipped distance.



# THE PHYSICAL INTERPRETATION OF WAVE MECHANICS

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**ABSTRACT.** The object of this paper is to give an account of the fundamental principles of wave mechanics in a manner which shall make clear the physical significance of all the quantities and processes involved. The principles are illustrated by discussions of the propagation of free electric waves in uniform electromagnetic fields and of bound electric waves in the hydrogen atom. The paper concludes with relativistic wave mechanics (prior to the work of Dirac and Darwin) and a short account of the Compton effect.

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# LIST OF SYMBOLS

$A$ Fermi's coefficient (§ 6·7)	$s$ strength of Hertzian doublet (§ 6)
$A$ electromagnetic vector potential (E.M.U.)	$S$ bounding surface
$a_1, a_2$ Dirac's coefficients (§ 6)	$t$ time
$a_n$ { coefficient in Sonine's polynomial (§ 5·2)	$T_n^n(n)$ Sonine's polynomial
$a_n$ { radius of Bohr orbit (§ 6·2)	$U$ proportional to potential of "quantum force"
$a_{len}$ matrix component of $A$ grad $\psi$	$V$ electrostatic potential (E.S.U.)
$a$ vector amplitude of $A$ (§ 7·4)	$u_1, u_2, \dots$ wave functions omitting time factor
$c$ velocity of light	$v$ velocity of electron
$E_{12}$ energy radiated in a transition (§ 6·7)	$W$ total energy of electron
$E$ electric intensity (E.S.U.)	$x, y, z$ Cartesian coordinates
$E$ energy of equivalent quantum (§ 7·4)	$z, R, \phi$ cylindrical coordinates
$-e$ electronic charge (E.S.U.)	$r, \theta, \phi$ spherical coordinates
$F$ strength of electrostatic field (§ 4·1)	$a$ acceleration of electron (§ 6·5)
$f$ momentum of equivalent quantum (§ 7·4)	$a$ modulus of $\psi$ (§ 3)
$H$ magnetic intensity (E.M.U.)	$\beta$ proportional to argument of $\psi$
$h$ Planck's constant	$\gamma$ reciprocal of radius of Bohr's ground orbit
$L$ Lagrangian function	$\epsilon$ $\sqrt{(-1)}$
$l_1, l_2, l_3$ direction cosines	$\kappa$ parameter measuring concentration of wave packets (§§ 4·2, 4·3) (cms.)
$M$ mass carried by waves (§ 3·2)	$\kappa$ parameter in wave eq. (§ 5) (cms. <sup>-1</sup> )
$M$ magnetic moment of atom	$\lambda$ wave-length (§§ 1, 2)
$m$ mass of electron	$\lambda + 1$ azimuthal quantum no. (§ 5·2)
$n$ a unit vector (§ 7·4)	$\Lambda$ Lagrangian function for electron (§ 7·1)
$n$ a quantum number (§ 5·2)	$\mu$ equatorial quantum no.
$N$ Rydberg constant	$\nu$ frequency
$p$ a positive integer (§ 5·2)	$\rho$ volume density of charge (E.S.U.)
$p$ momentum of electron (§§ 1, 2)	$\sigma$ current density (E.M.U.)
$p_{len}$ polarisation	$d\tau$ element of volume
$Q$ charge carried by waves	$\psi$ wave function
$q$ velocity of charge carried by waves	$\omega$ $eH/2mc$ , Larmor rotation (§§ 4·3, 5·5)
$R =  r - r' $ (§ 6·1)	$\omega = 2\pi\nu$ (§ 6)
$r$ position vector	$\nabla$ vector operator
$s = (h/2\pi) \log (\text{wave function } \psi)$ (§ 2·2)	

Vectors,  $A$ , are printed in Clarendon type. Their components are  $A_1, A_2, A_3$ . The scalar product of  $A$  and  $B$  is  $A \cdot B$ . The vector product is  $A \wedge B$ .

Dots ( $\dot{a}$ ) denote differentiation with respect to time. Asterisks (\*) denote the conjugate complex quantity. Bars ( $\bar{a}$ ) are used for the coordinates of mean position. Primes (') refer to points in the domain of integration (§ 6), or denote differentiation with respect to  $x$  (§ 5).

## § 1. INTRODUCTION: LIGHT CONSIDERED AS QUANTA AND ELECTRONS CONSIDERED AS WAVES

THE two primary elements of atomic physics—the quantum and the electron—possess a remarkable similarity in the properties with which they are credited. Indeed Beck\* has even suggested that with every property of the electron there should be correlated some property of the quantum, so that, for example, we might associate the spin of an electron and the circular polarisation of a quantum. But the most arresting feature of this analogy is the absence of any compelling evidence for the existence either of free quanta or of free electrons.

\* G. Beck, "Über einige Folgerungen aus dem Satz von der Analogie zwischen Lichtquant und Electron," *Zeits. f. Physik*, 43, 658–74 (1927).

Modern quantum theory\* is content with the quantisation of the optical energy transferred in processes of emission and absorption, and contemplates with equanimity the possibility that free radiation may be governed only by classical laws of continuity. It will be shown in this paper that a similar self-denying ordinance may be welcomed in the theory of electrons.

In the first place, it must be noted that any direct experiments, such as Millikan's, which purport to measure the electronic charge, are, in reality, competent to determine only the magnitudes of the electrical charges which can be absorbed or emitted by atoms. These experiments can establish at most that a quantity of negative electricity associated with an atom is a multiple of the unit which we call the "electronic charge": they necessarily fail to provide information regarding the atomicity or continuity of free electricity. It is true that such experiments as those conducted by Richardson and Brown appear to determine the distribution of velocity among free electrons and hence imply the atomicity of free electricity, but these experiments can also be interpreted without postulating the existence of free electrons.

In the second place, it is significant that Schrödinger's wave mechanics, which obliterates the discrete structure of a system of free electrons, preserves most carefully the integral character of the number of electronic charges bound to an atom. Since this theory does not require free electricity to be atomic in structure, an immediate exercise of Occam's razor frees us from the burden of such an assumption.

The old quantum theory replaced waves of light by quanta of optical energy. The new wave mechanics replaces quanta of electrical charge by waves of electricity, and replaces an atmosphere of free electrons by a spectral band of waves. In fact the fundamental equations of wave mechanics may be developed in such a way as to exhibit the transition from electrons to waves of electricity as a process which is reciprocal to the transition from waves of light to quanta with which we have been familiarised by the older quantum theory. That theory replaced a plane wave of light of frequency  $\nu$  and wave-length  $\lambda$  by a stream of quanta each of energy  $W = h\nu$  and of momentum  $p = h/\lambda$ ,  $h$  being Planck's constant. In a similar manner the new wave mechanics replaces a uniform stream of electrons each of energy  $W$  and of momentum  $p$  by a plane wave of electricity of frequency  $\nu = W/h$  and of wave-length  $\lambda = h/p$ .

A wealth of experimental evidence† is even now being accumulated in support of this theory. It has been shown that "a stream of electrons" may be scattered by amorphous films, diffracted by crystalline films or ruled gratings, and reflected from crystalline faces just as if it were a pencil of very hard X-rays. Moreover there is a fair numerical agreement between the experimental results and the predictions based upon the value of the wave-length given by the formula  $\lambda = h/p$ .

The analytical development of wave mechanics will take one of two parallel

\* A. S. Eddington, *The Internal Constitution of the Stars*, § 41 (1926).

† B. L. Worsnop, "Note on the Transmission of Cathode Rays through Thin Films," *Proc. Phys. Soc.* 40, 281-4 (1928).

routes according to the expression of the momentum  $p$  and energy  $W$  in the Newtonian form  $mv$  and  $\frac{1}{2}mv^2$ , or in the Einsteinian form  $mv(1 - v^2/c^2)^{-\frac{1}{2}}$  and  $mc^2(1 - v^2/c^2)^{-\frac{1}{2}}$ ,  $m$  being the rest-mass and  $v$  the velocity of the electron. The two values obtained for the wave velocity  $\lambda v = W/p$  are respectively  $\frac{1}{2}v$  and  $c^2/v$ . In spite of the inadmissible character of the first value some consideration will be devoted to "classical" wave mechanics for the following reasons:

1. The differential equations of this theory are easier to formulate, interpret and solve.
2. They provide a good first approximation to the equations of "relativistic" wave mechanics.
3. There is still a discussion as to the proper form to be taken by the equations of relativistic wave mechanics, e.g. Dirac and Darwin employ four complex wave formations and find difficulties in putting the wave equations in covariant form.

## §2. THE FUNDAMENTAL EQUATIONS OF CLASSICAL WAVE MECHANICS

Since the wave theory of electricity receives experimental support from observations on free electricity it is worth while to investigate whether it can be harmonised with the old quantum theory of bound electricity which has been so successful in dealing with series spectra. But as soon as we endeavour to picture an atom in a stationary state as a positive nucleus surrounded by stationary waves of electricity we are again confronted by all the old difficulties associated with radiation from the moving charges which we imagine to be carried by the waves. One way out of these difficulties has been indicated by Lorentz\*, who has suggested that the bound electricity might be distributed continuously around the "electronic orbit," so that the motion of the electric charge would give rise to a steady current emitting no radiation.

Now we can easily imagine a system of waves whose charge is concentrated near an "electronic orbit," but it is difficult to imagine any system of waves, *all of the same character*, giving rise to a steady distribution of electric charge. This difficulty may be evaded by introducing two systems of waves superimposed on one another and with suitable relations between their phases and amplitudes. We should thus obtain a state of affairs similar to the regime prevailing in a plane wave of light when the joint effect of the electric and magnetic waves is to produce a uniform distribution of optical energy.

### 2.1. Construction of the Wave Equation.

To give an analytical form to these assumptions, consider first the simplest type of wave—plane monochromatic waves of uniform amplitude. Let the two wave functions be the real and imaginary parts of

$$\psi = A \exp 2\pi i \{(l_1 x + l_2 y + l_3 z)/\lambda - \nu t\}.$$

\* H. A. Lorentz, *Lectures on Theoretical Physics*, 2, 329-33 (1927).

This double wave system is to replace a stream of electrons, each having energy  $W = h\nu$  and components of momentum

$$p_1 = l_1 h/\lambda, \quad p_2 = l_2 h/\lambda, \quad p_3 = l_3 h/\lambda.$$

Hence, if  $\mathbf{p}$  is the vector representing the momentum, and  $\nabla$  the vector operator with components  $\partial/\partial x, \partial/\partial y, \partial/\partial z$ , then

$$(h/2\pi i) \nabla \psi = \mathbf{p}\psi \quad \dots\dots(2.11),$$

$$\text{and} \quad (-h/2\pi i) \partial\psi/\partial t = W\psi \quad \dots\dots(2.12).$$

Since, for free electrons of mass  $m$  and velocity  $\mathbf{v}$ ,

$$\mathbf{p} = m\mathbf{v}, \quad W = \frac{1}{2}mv^2, \quad \text{and} \quad p^2 = 2mW \quad \dots\dots(2.13),$$

therefore we find that the corresponding wave functions satisfy the equation

$$h \cdot \nabla^2 \psi + 4\pi m i \cdot \partial\psi/\partial t = 0 \quad \dots\dots(2.14).$$

Secondly, consider an electron moving under the influence of an electromagnetic field. Let  $V$  be the electrostatic potential and  $\mathbf{A}$  the electromagnetic vector potential. If  $-e$  is the electronic charge in electrostatic units we have the relations

$$\mathbf{p} = m\mathbf{v} - e\mathbf{A}/c, \quad W = \frac{1}{2}mv^2 - eV \quad \dots\dots(2.15),$$

$$\text{and} \quad (\mathbf{p} + e\mathbf{A}/c)^2 = 2m(W + eV) \quad \dots\dots(2.16).$$

It will accordingly be assumed that the equation for electric waves which interact with an electromagnetic field is

$$\frac{1}{2m} \left\{ \frac{e}{c} \mathbf{A} + \frac{h}{2\pi i} \nabla \right\}^2 \cdot \psi = - \frac{h}{2\pi i} \frac{\partial\psi}{\partial t} + eV\psi \quad \dots\dots(2.17).$$

## 2.2. Lagrangian Form of the Wave Equation†.

This equation (2.17), judged according to its analytical form, is not a wave equation but a diffusion equation, and in consequence it cannot be deduced from a Lagrangian function. But this difficulty can be evaded by considering only those wave functions which are simply periodic in time, so that, if  $\nu$  is the frequency,

$$- \frac{h}{2\pi i} \frac{\partial\psi}{\partial t} = h\nu\psi.$$

If we write  $\psi = \exp(2\pi i s/h)$ ,  $\psi^* = \exp(-2\pi i s^*/h)$ , using the asterisk to denote the conjugate complex quantity, and finally

$$L/\psi^*\psi = (h\nu + eV) - (e\mathbf{A}/c + \text{grad } s)(e\mathbf{A}/c + \text{grad } s^*)/(2m) \quad \dots\dots(2.21),$$

it is easily verified that the wave equation (2.17) for wave functions with frequency  $\nu$  is equivalent to the Lagrangian equation

$$\delta \int L dx dy dz = 0,$$

the variations being taken with respect to  $\psi^*$ .

† So much of the work is due to Schrödinger that only a general reference to his collected papers, now published in an English translation, can be given here.

To interpret this Lagrangian function, introduce the scalar  $\rho$  and the vector  $\sigma$  defined by the equations

$$\rho = -\partial L/\partial V = -e\psi^*\psi \quad \dots\dots(2.22),$$

$$\sigma = +\partial L/\partial \mathbf{A} = (he/4\pi mc)(\psi^* \text{grad } \psi - \psi \text{ grad } \psi^*) - (e/mc^2) \mathbf{A} \rho \quad \dots(2.23).$$

If we agree that the vector potential is to satisfy the condition  $\text{div } \mathbf{A} = 0$ , it follows from the wave equation (2.17) that

$$c \text{ div } \sigma + \partial \rho / \partial t = 0 \quad \dots\dots(2.24),$$

so that  $\rho$  and  $\sigma$  satisfy the equation of continuity.

We may now write  $L$  in the form

$$\{h\nu\psi^*\psi - (h^2/8\pi^2m) \text{grad } \psi \cdot \text{grad } \psi^*\} + \mathbf{A} \cdot \sigma - V\rho + (e^2/2mc^2) A^2\psi^*\psi \quad \dots(2.25).$$

The Lagrangian function for the electromagnetic field is

$$\left. \begin{array}{l} L_0 = (E^2 - H^2)/8\pi, \\ \text{where } \mathbf{E} = -\text{grad } V - \partial \mathbf{A}/\partial t \quad (\text{E.S.U.}) \\ \text{and } \mathbf{H} = \text{curl } \mathbf{A} \quad (\text{E.M.U.}) \end{array} \right\} \quad \dots\dots(2.26).$$

The interaction of the electromagnetic field and the electric waves may be deduced from the complete Lagrangian function  $L_0 + L$ . Variation with respect to  $\psi^*$  yields, as before, the wave equation (2.17). Variation with respect to  $V$  and  $\mathbf{A}$  yields Maxwell's equations

$$\text{div } \mathbf{E} = 4\pi\rho, \quad \text{curl } \mathbf{H} - \partial \mathbf{E}/\partial t = 4\pi\sigma \quad \dots\dots(2.27).$$

For this reason  $\rho$  is taken to be the volume density of the charge carried by the electric waves, while  $\sigma$  is taken to be the current density (E.M.U.).

Returning to the expression for the Lagrangian function (2.25) we note that the usual terms expressing the interaction of the charge and field, namely  $(\mathbf{A} \cdot \sigma - V\rho)$ , are supplemented by an additional small term  $(e^2/2mc^2) A^2\psi^*\psi$ , while the remaining terms,  $h\nu\psi^*\psi$  and  $(h^2/8\pi^2m) \text{grad } \psi \cdot \text{grad } \psi^*$ , are most easily interpreted as the volume densities of the kinetic and potential energy carried by the electric wave.

### §3. CLASSICAL ELECTRON THEORY AS A FIRST APPROXIMATION TO WAVE MECHANICS

The preceding section was devoted to the construction of the fundamental equations of classical wave mechanics. In this section it will be shown that, to a first approximation, the motion of electric charge as determined by the wave equation agrees with the predictions of the classical electron theory. The main theorems required are due to Madelung and Ehrenfest.

#### 3.1. Madelung's Hydrodynamical Form of the Wave Equation†.

Since the wave function  $\psi$  is a complex quantity, we shall write

$$\psi = \alpha \exp(2\pi m i \beta / h) \quad \dots\dots(3.11),$$

where  $\alpha$  and  $\beta$  are both real quantities. Then we find that

$$\rho = -e\alpha^2 \quad \dots\dots(3.12),$$

† E. Madelung, "Quantentheorie in hydrodynamischer Form," *Zeits. f. Physik*, **40**, 322-6 (1927); E. H. Kennard, "On the Quantum Mechanics of a System of Particles," *Phys. Rev.* **31**, 876-90 (1928).

and  $c\sigma = \rho (\text{grad } \beta + e\mathbf{A}/mc) = \rho\mathbf{q}$ , say .....(3.13).

The wave equation for the complex function  $\psi$  yields two simultaneous equations for the real functions  $\alpha$  and  $\beta$ , namely, the equation of conservation,

$$\text{div}(\rho\mathbf{q}) + \partial\rho/\partial t = 0 \quad \text{.....(3.14),}$$

and the "hydrodynamical equation,"

$$\partial\beta/\partial t + \frac{1}{2}q^2 - eV/m = (h^2\nabla^2\alpha)/(8\pi^2m^2\alpha) \quad \text{.....(3.15).}$$

This equation may be interpreted in two ways. First, let

$$U = (h^2/8\pi^2m^2) (\nabla^2\alpha/\alpha) \quad (\text{cm.}^2/\text{sec.}^2) \quad \text{.....(3.16).}$$

Then by taking the gradient of equation (3.15) we obtain the result

$$m\{\dot{\mathbf{q}} + (\mathbf{q} \cdot \nabla) \mathbf{q}\} = -e\mathbf{E} + e[\mathbf{H} \wedge \mathbf{u}/c] + m \text{grad } U \quad \text{.....(3.17).}$$

Hence the electric charge carried by the waves moves as if it were carried by a perfect liquid in which the ratio of the electric density to the mass density is  $(-e/m)$ , the usual electric and magnetic forces being supplemented by a "quantum force," of magnitude

$$\mathbf{F} = -(\rho m/e) \text{grad } U, \text{ per unit volume.}$$

Secondly, writing the equation (3.15) in the Hamiltonian form

$$\partial\beta/\partial t + \frac{1}{2}\{\text{grad } \beta + e\mathbf{A}/mc\}^2 = U + eV/m \quad \text{.....(3.18),}$$

we see that  $m\beta$  is the "action function" for an electron subjected to a "quantum force,"  $-m \text{grad } U$ , in addition to the usual electromagnetic forces. It follows that  $\mathbf{q}$  would be the velocity of the electron at any point. Hence a system of electrons under the action of the usual electromagnetic forces plus the "quantum force" would move along the paths of flow of the current carried by the associated electric wave.

### 3.2. Ehrenfest's Form of the Wave Equation\*.

Let us consider solutions of the wave equation for which there exists a closed surface  $S$  over which the normal component of the current velocity  $\sigma/\rho = \mathbf{q}/c$  is everywhere zero. The total quantity of electricity within this surface is

$$Q = \int \rho d\tau,$$

$d\tau$  being an element of volume, and on the basis of Madelung's theorem we shall call

$$M = (-m/e) Q,$$

the total "mass" associated with the waves inside  $S$ . The position vector of the "mass-centre" is defined by the equations

$$Q(\bar{x}, \bar{y}, \bar{z}) = \int (x, y, z) \rho d\tau.$$

We proceed to find expressions for the total momentum,  $Md\bar{x}/dt$ , ..., and the total effective force,  $Md^2\bar{x}/dt^2$ , ..., associated with the waves inside  $S$ .

\* P. Ehrenfest, *Zeit. f. Physik*, 45, 455-7 (1927); A. E. Ruark, "...The Force Equation and the Virial Theorem in the New Mechanics," *Phys. Rev.* 31, 533-8 (1928).

Since  $\text{div} (x\sigma) = x \text{div} \sigma + \sigma_1^*$ , .....(3.21),  
 therefore 
$$\left. \begin{aligned} Qd\bar{x}/dt &= \int x \rho d\tau = -c \int x \text{div} \sigma \cdot d\tau \\ &= c \int \sigma_1 d\tau - c \int x (\sigma \cdot dS) \end{aligned} \right\} \text{.....(3.22),}$$

the last integral being taken over the surface  $S$ . Since the normal component of  $\sigma$  vanishes over  $S$ , the total momentum

$$Md\bar{x}/dt = -(mc/e) \int \sigma_1 d\tau \text{.....(3.23).}$$

To calculate the total effective force consider the  $x$ -component of the vector  $\rho E + (\sigma \wedge H)$ . This is equal to

$$-\rho \frac{\partial V}{\partial x} - \frac{\rho}{c} \frac{\partial A_1}{\partial t} + \sigma_2 \left\{ \frac{\partial A_2}{\partial x} - \frac{\partial A_1}{\partial y} \right\} - \sigma_3 \left\{ \frac{\partial A_1}{\partial z} - \frac{\partial A_3}{\partial x} \right\}.$$

In this expression substitute

$$A = (mc^2/e\rho) \sigma - (mc/e) \text{grad } \beta,$$

$$V = (m/e) \partial \beta / \partial t + (mc^2 \sigma^2 / 2e\rho^2) - (m/e) U;$$

from equations (3.13) and (3.15). We thus obtain

$$-(mc/e) \dot{\sigma}_1 + (\rho m/e) \partial U / \partial x - (mc^2/e) I,$$

where

$$I = \frac{\partial}{\partial x} \left\{ \frac{\sigma_1^2}{\rho} \right\} + \frac{\partial}{\partial y} \left\{ \frac{\sigma_1 \sigma_2}{\rho} \right\} + \frac{\partial}{\partial z} \left\{ \frac{\sigma_1 \sigma_3}{\rho} \right\}.$$

The integral of  $I$  over the volume enclosed by  $S$  is evidently zero by Green's Theorem and the definition of  $S$ . Hence

$$Md^2 \bar{x} / dt^2 = -(mc/e) \int \dot{\sigma}_1 d\tau = \int \{ \rho E_1 + (\sigma \wedge H)_1 - (\rho m/e) \partial U / \partial x \} d\tau \text{... (3.24).}$$

Thus the effective force on the mass-centre is the sum of the electromagnetic forces and the "quantum force" acting on the charge and current carried by the wave inside  $S$ . Hence the bulk motion of waves concentrated in small regions of space would be the same as the motion of an electron subjected to the same forces.

It only remains to note that the quantum force will only be of sensible magnitude on the boundaries of a beam where  $\alpha$  is varying rapidly.

#### §4. ILLUSTRATIONS OF THE DISTORTION OF ELECTRIC WAVES BY ELECTROMAGNETIC FIELDS

In the preceding section the equivalence of the classical electron theory and of classical wave mechanics was established in a general way. This general theorem will now be illustrated by a number of particular examples drawn from the work of Schrödinger and Darwin and presented here in a simplified form based on Madelung's theorem.

##### 4.1. Uniform Electrostatic Field†.

Let the potential of the field be  $V = -Fx$ . Assume provisionally that the wave carries a charge of uniform density  $\rho = -e\alpha^2$ , and a current with components of velocity

$$q_1 = \partial \beta / \partial x = u - eFt/m \text{.....(4.11),}$$

$$q_2 = \partial \beta / \partial y = v \text{.....(4.12)}$$

\*  $\sigma_1, \sigma_2, \sigma_3$  are the components of  $\sigma$ .

† C. G. Darwin, "Free Motion in the Wave Mechanics," *Proc. R. S. A*, 117, 258-93 (1927).



(see equations (3.12) and (3.13)), i.e. the same values as would be acquired by an electron projected initially with components  $u$  and  $v$ .

From the Hamiltonian form of the wave-equation (3.18) we find that

$$\partial\beta/\partial t = -eFx/m - \frac{1}{2}\{u^2 + v^2 - 2eFut/m + e^2F^2t^2/m^2\} \dots\dots(4.13).$$

These three equations ((4.11), (4.12) and (4.13)) are consistent and possess the solution

$$\beta = u(x - \frac{1}{2}ut) - eFxt/m + v(y - \frac{1}{2}vt) + eFut^2/2m - e^2F^2t^3/6m^2 \dots(4.14).$$

Hence the provisional assumptions made above are justified.

#### 4.2. Linear Oscillator\*.

The wave which corresponds to an electron moving in a field of potential  $V = -2\pi^2\nu^2mx^2/e$  will now be investigated. At time  $t$ , the electron would have a displacement  $x = a \cos 2\pi\nu t$ . Accordingly it will be assumed that the wave is concentrated around the point which would be occupied by the electron, and that its amplitude is

$$\alpha = \exp \frac{(x - a \cos 2\pi\nu t)^2}{-2\kappa^2} \dots\dots(4.21).$$

The Hamiltonian equation (3.18) now becomes

$$\begin{aligned} \partial\beta/\partial t + \frac{1}{2}(\partial\beta/\partial x)^2 &= x^2 \{(\hbar^2/8\pi^2m^2\kappa^4) - 2\pi^2\nu^2\} \\ &\quad - (\hbar^2/8\pi^2m^2\kappa^4) \{\kappa^2 - a^2 \cos^2 2\pi\nu t + 2ax \cos 2\pi\nu t\} \dots\dots(4.22). \end{aligned}$$

Adjusting  $\kappa$  so that the first term vanishes we find that a solution is

$$\begin{aligned} \beta &= -2\pi\nu ax \sin 2\pi\nu t + f(t) \\ \text{where } f(t) &= -\hbar vt/2m + \frac{1}{2}\pi\nu a^2 \sin 4\pi\nu t \end{aligned} \dots\dots(4.23).$$

We still have to show that these expressions for  $\alpha$  and  $\beta$  yield consistent values of the charge and current. From equation (3.13) we find that

$$\begin{aligned} c\sigma_1 &= -e\alpha^2 \cdot \partial\beta/\partial x \\ &= 2\pi\nu a e \alpha^2 \sin 2\pi\nu t \end{aligned} \dots\dots(4.24),$$

whence

$$c \operatorname{div} \sigma = 2e\alpha\dot{\alpha} = -\dot{\rho},$$

which is the condition of continuity required. Thus it has been shown that, corresponding to an electron vibrating in a linear oscillator, there exists a wave concentrated in a region around the position of the electron with dimensions of the order of

$$\kappa = \sqrt{(\hbar/4\pi^2\nu m)} \text{ cms.}$$

#### 4.3. Uniform Magnetic Field†.

A uniform magnetic field of strength  $H$  directed along the  $z$ -axis has the vector potential whose components in cylindrical coordinates ( $z, R, \phi$ ) are

$$A_1 = 0, \quad A_2 = 0, \quad A_3 = \frac{1}{2}HR.$$

The Hamiltonian wave equation is

$$\partial\beta/\partial t + \frac{1}{2}(\partial\beta/\partial R)^2 + \frac{1}{2}(\partial\beta/R\partial\phi + \omega R)^2 = \hbar^2\nabla^2\alpha/8\pi^2m^2\alpha \dots\dots(4.31),$$

where

$$\omega = eH/2mc \dots\dots(4.32).$$

\* E. Schrödinger, "Der stetige Übergang von der Mikro- zur Makro-mechanik," *Die Naturwissenschaften*, 28, 664-6 (1926).

† *Loc. cit. sup.*

An electron in the same field would describe a circle  $R = a$  with angular velocity  $2\omega$ . Hence we shall assume provisionally that the corresponding wave is concentrated around this moving point with amplitude

$$\alpha = \exp \frac{\{R^2 - 2Ra \cos(\phi - 2\omega t) + a^2\}}{-2\kappa^2} \dots\dots(4.33).$$

It follows that  $\nabla^2 \alpha / \alpha = -2/\kappa^2 + \{R^2 - 2Ra \cos(\phi - 2\omega t) + a^2\}/\kappa^4$ .

Adjusting the value of  $\kappa$  so that the terms in  $R^2$  disappear from the Hamiltonian equation (4.31), we find that a solution is

$$\beta = -(h\omega t/2\pi m) + a\omega R \sin(\phi - 2\omega t), \quad 2\pi\kappa^2 = h/m\omega \dots\dots(4.34).$$

From equation (3.13) it follows that the current carried by the wave has velocity components

$$q_1 = 0, \quad q_2 = \partial\beta/\partial R = a\omega \sin(\phi - 2\omega t)$$

and

$$q_3 = \partial\beta/R\partial\phi + eA_3/mc = a\omega \cos(\phi - 2\omega t) + \omega R \dots\dots(4.35).$$

It is easily verified that the components of the current density  $\rho q_1, \rho q_2, \rho q_3$  satisfy the equation of continuity and hence the consistency of our provisional solution is demonstrated.

## §5. THE STATIONARY STATES OF AN ATOM

In § 2 the introduction of a complex wave function  $\psi = \xi + i\eta$  was briefly justified on the ground that the joint action of both the real wave functions  $\xi$  and  $\eta$  would be required to produce a non-radiating distribution of electric charge in an atom. In this section the wave functions associated with an atom in a stationary state will be examined in detail. The nuclear charge will be supposed to be  $e$  and the electrostatic potential due to this charge to be  $e/r$ . For waves of frequency  $\nu$ , corresponding to electrons of total energy  $W = h\nu$ , the wave equation (2.17) is

$$\nabla^2 \psi + (8\pi^2 m/h^2)(W + e^2/r)\psi = 0 \dots\dots(5.01).$$

Since the energy of an electron in a closed orbit would be negative, we write

$$\left. \begin{aligned} h\kappa &= \sqrt{(-8\pi^2 m W)} \\ h^2 \gamma &= 4\pi^2 m e^2 \end{aligned} \right\} \dots\dots(5.02),$$

and

so that the wave equation becomes

$$\nabla^2 \psi = (\kappa^2 - 2\gamma r^{-1})\psi \dots\dots(5.03).$$

### 5.1. The Existence of Discrete Energy Levels.

It will now be shown that the whole of the waves associated with an atom in a stationary state has the same frequency and that the possible frequencies in different stationary states form a discrete series.

Let  $\kappa_1$  and  $\kappa_2$  be two possible values of  $\kappa$  corresponding to the possible values of the frequency, and let  $\psi_1$  and  $\psi_2$  be corresponding solutions of the wave equation (5.03). Then it follows that

$$\psi_2^* \nabla^2 \psi_1 - \psi_1 \nabla^2 \psi_2^* = (\kappa_1^2 - \kappa_2^2) \psi_2^* \psi_1.$$

Integrate throughout a sphere of radius  $r$ . Then, by Green's Theorem,

$$(\kappa_1^2 - \kappa_2^2) \int \psi_2^* \psi_1 \cdot d\tau = \int (\psi_2^* \text{grad } \psi_1 - \psi_1 \text{grad } \psi_2^* \cdot dS),$$

$d\tau$  being a volume element and  $dS$  a surface element. If we agree that the wave functions are to behave like  $r^{-1}$  as  $r$  tends to infinity, we find that the volume integral of  $\psi_2^* \psi_1$  throughout all space is zero unless  $\kappa_1 = \kappa_2$  when it is obviously positive.

Now suppose that the possible range of frequencies to be found in stationary states includes a band extending from  $\nu_1$  to  $N$ , and that the corresponding range of values of  $\kappa$  extends from  $\kappa_1$  to  $K$ . Consider the volume integral

$$\int_{\infty} \psi_2^* \psi_1 d\tau = f(\kappa_2)$$

as a function of  $\kappa_2$ . When  $K > \kappa_2 > \kappa_1$ ,  $f(\kappa_2) = 0$ ; when  $\kappa_2 = \kappa_1$ ,  $f(\kappa_2) > 0$ ; i.e. there is a discontinuity at  $\kappa_2 = \kappa_1$  although  $\psi_2^*$  and the volume integral are continuous functions of  $\kappa_2$ . Hence the possible range of frequencies cannot include a band, but must form a discrete series; and the same holds of the possible range of  $\kappa$  or  $W$ .

Let  $\nu_1$  and  $\nu_2$  be two terms of this series and let  $u_1 \exp(-\omega_1 t)$  and  $u_2 \exp(-\omega_2 t)$ , ( $\omega = 2\pi\nu$ ), be corresponding solutions of (5.03),  $u_1$  and  $u_2$  being independent of  $t$ . Suppose that waves of both frequencies could be present in a stationary state. Then the complete wave function would be of the form

$$\psi = u_1 \exp(-\omega_1 t) + u_2 \exp(-\omega_2 t),$$

and the density of the charge carried by the waves would be

$$\rho = -e\psi^*\psi = -e(u_1^*u_1 + u_2^*u_2) - eu_2^*u_1 \exp(\omega_2 - \omega_1)t - eu_1^*u_2 \exp(\omega_1 - \omega_2)t.$$

Hence upon the static charge of density  $-e(u_1^*u_1 + u_2^*u_2)$  would be superimposed a charge whose density fluctuates with frequency  $|\nu_2 - \nu_1|$ . This fluctuation would give rise to radiation of the same frequency, the electromagnetic field of the radiation would react on the electric wave system and the stationary state would be destroyed. Hence to preserve an atom in a stationary state all the waves must have the same frequency.

Thus it has been shown that the quantisation of the energy is a direct consequence of the form of the equation satisfied by the wave function  $\psi$ .

### 5.2. The Values of the Discrete Energy Levels.

In order to determine explicitly the permissible values of the frequency we note that the wave equation (5.03), when written in spherical polar coordinates  $(r, \theta, \phi)$ , possesses elementary solutions of the form

$$u(\lambda, \mu) = \exp(-\kappa r + \lambda \log r \pm i\mu\phi) \cdot f(2\kappa r) \cdot P_{\lambda}^{\mu}(\cos \theta) \quad \dots\dots(5.21),$$

where  $f(x)$  satisfies the equation

$$xf'' + (2\lambda + 2 - x)f' - (\lambda + 1 - \gamma/\kappa)f = 0 \quad \dots\dots(5.22).$$

This equation possesses only one solution which is valid in the vicinity of the origin,  $x = 0$ , and which takes the value unity at that point. This solution may be represented by the series

$$f(x) = 1 + a_1x + a_2x^2/2! + \dots + a_nx^n/n! + \dots \quad \dots\dots(5.23)$$

in which the coefficients are connected by the recurrence relation

$$(n + 2\lambda + 2)a_{n+1} = (n + \lambda + 1 - \gamma/\kappa)a_n \quad \dots\dots(5.24).$$

Now the only wave functions which are physically admissible are those which are single-valued and finite throughout all space. A reference to equation (5.21) shows that to satisfy these conditions  $\mu$  must be a positive integer or zero, while  $\lambda$  must be a positive integer or zero and not less than  $\mu$ . It will now be shown that there is also a limitation on the possible values of  $\gamma/\kappa$ .

If  $(\gamma/\kappa - \lambda)$  is a positive integer  $n$ , the series (5.23) will terminate with the term  $a_n x^n/n!$ . But if  $(\gamma/\kappa - \lambda)$  is not a positive integer, the series (5.23) will not terminate. Since the ratio

$$\frac{a_{n+1}}{a_n} = \frac{n + 2\lambda + 2}{n + \lambda + 1 - \gamma/\kappa}$$

tends to unity as  $n \rightarrow \infty$ , the series converges uniformly for all finite values of  $x$  and behaves like  $\exp x$  as  $x \rightarrow \infty$ . Hence, as  $r \rightarrow \infty$ , the wave function  $u(\lambda, \mu)$  behaves like  $\exp(\kappa r + \lambda \log r)$  and therefore increases without limit. Therefore  $(\gamma/\kappa - \lambda)$  must be a positive integer,  $n$ .

Under these circumstances

$$-W = -h\nu = \hbar^2 \kappa^2 / 8\pi^2 m = \frac{\hbar^2 \gamma^2}{8\pi^2 m (\lambda + n)^2} = \frac{2\pi^2 m e^4}{\hbar^2 (\lambda + n)^2} \dots\dots(5.25)$$

and  $f(x)$  is a multiple of Sonine's polynomial  $T_{2\lambda+1}^{n-1}(x)$ , which is given by the series

$$T_m^n(x) = \frac{x^n}{(m+n)!n!} - \frac{x^{n-1}}{(m+n-1)!(n-1)!} + \dots + \frac{(-)^{p+n} x^p}{(m+p)!(n-p)!p!} - \dots + \frac{(-)^n}{m!n!} \dots\dots(5.26).$$

Since the value of the Rydberg constant is

$$N = 2\pi^2 m e^4 / \hbar^3,$$

the permissible values of the frequency are given by the equation

$$-v = N/(\lambda + n)^2 \dots\dots(5.27).$$

### 5.3. Atomic Dimensions.

That part of the wave function  $u(\lambda, \mu)$ , equation (5.21), which depends on  $r$  may be written as

$$\exp(-\kappa r + \lambda \log r) \cdot T_{2\lambda+1}^{n-1}(2\kappa r).$$

When Sonine's polynomial is expanded in powers of  $(2\kappa r)$  the wave function consists of the sum of a number of terms of the form

$$A \exp(-\kappa r) \cdot r^{\lambda+p}, \quad (p = 0, 1, 2, \dots, n-1).$$

Such a term reaches a maximum value when  $\kappa r = \lambda + p$ , and then decreases rapidly as  $r$  increases. Hence, when

$$r > (\lambda + n)/\kappa = (\lambda + n)^2/\gamma,$$

all the terms are decreasing in magnitude.

In Bohr's theory the radius of an orbit of energy  $(-h\nu)$  was  $e^2/(-2h\nu)$ . But from equations (5.02) and (5.25)

$$-2h\nu = \gamma e^2 (\lambda + n)^{-2}$$

on the present theory. Hence the radius of Bohr's orbit is  $(\lambda + n)^2/\gamma$ . Therefore we see that outside a sphere of this radius the magnitude of the wave function rapidly diminishes. Hence the charge and current carried by the waves are confined to sphere with a radius of the order of magnitude of the corresponding Bohr orbit.

#### 5.4. The Bohr Magneton\*.

Consider those stationary states of the atom for which the frequency of oscillation has the greatest possible values. If we take  $\lambda + n = 1, 2$ , the corresponding wave functions are those given below.

$$\begin{aligned} \lambda + n = 1; \text{ i.e. } n = 1, \lambda = 0, \mu = 0, \\ u = \exp(-r/\gamma): \\ \lambda + n = 2; \text{ i.e. } n = 2, \lambda = 0, \mu = 0, \\ u = (1 - 2r/\gamma) \exp(-2r/\gamma), \\ \text{or } n = 1, \lambda = 1, \mu = 0, \\ u = r \cos \theta \cdot \exp(-2r/\gamma), \\ \text{or } n = 1, \lambda = 1, \mu = \pm 1, \\ u = r \sin \theta \cdot \exp(-2r/\gamma \pm i\phi). \end{aligned}$$

In the first four cases the wave carries a static charge but no current. In the last case the two wave functions may be written as

$$\begin{aligned} \psi_1 &= f(r, \theta) \cdot \exp(i\phi - 2\pi i \nu t), \\ \psi_2 &= f(r, \theta) \cdot \exp(-i\phi - 2\pi i \nu t). \end{aligned}$$

Hence the most general wave function involving  $\phi$  for this energy level is

$$\psi = f(r, \theta) \exp(-2\pi i \nu t) \{c_1 \exp i(\phi + \alpha_1) + c_2 \exp -i(\phi + \alpha_2)\},$$

where  $c_1, c_2, \alpha_1, \alpha_2$  are real.

If the total charge carried by the wave is  $-e$ , it follows from equation (2.81) that

$$2\pi (c_1^2 + c_2^2) \int_0^\infty r^2 dr \int_0^\pi f^2 \sin \theta d\theta = 1.$$

The current has the direction of the  $\phi$ -coordinate, i.e. it flows in circles around the  $z$ -axis. The current density is, from equation (2.23),

$$- (he/2\pi mc) (c_1^2 + c_2^2) f^2 / (r \sin \theta).$$

The total magnetic moment due to a distribution of current with density  $\sigma$  at the point whose position vector is  $\mathbf{r}$  is

$$\mathbf{M} = \frac{1}{2} \int [\mathbf{r} \wedge \sigma] d\tau.$$

Hence in this case it follows that the magnetic moment is along the  $z$ -axis and of magnitude

$$\begin{aligned} (he/2mc) (c_1^2 + c_2^2) \int_0^\infty r^2 dr \int_0^\pi f^2 \sin \theta d\theta &= he/4\pi mc \\ &= 1 \text{ Bohr magneton.} \end{aligned}$$

Therefore the quantisation of the magnetic moment is a consequence of making the total charge of the waves equal to  $-e$ .

\* E. Fermi, "Quantum Mechanics and the Magnetic Moment of Atoms," *Nature*, 118, 876 (1926); V. Fock, "Zur Schrödingerscher Wellenmechanik," *Zeit. f. Physik*, 38, 242-50 (1926).

### 5.5. The Zeeman Effect.

Let us determine the change in the characteristic frequencies produced by the application of a magnetic field of uniform strength  $H$  along the  $z$ -axis. As in § 4, the components of the vector potential are

$$A_1 = 0, A_2 = 0, A_3 = \frac{1}{2}HR,$$

in cylindrical coordinates  $(z, R, \phi)$ . It follows from equation (2.17) that the wave equation is

$$\nabla^2\psi + \frac{2\pi eH}{hc} \frac{\partial\psi}{R\partial\phi} = -\frac{4\pi m\mu}{h} \frac{\partial\psi}{\partial t} - \frac{2\gamma}{r} \psi,$$

neglecting squares of  $H$ . Put  $\phi = \phi_1 + \omega t$ ,

where  $\omega = eH/2mc$ ,

and this equation becomes

$$\nabla_1^2\psi = -\frac{4\pi m\mu}{h} \frac{\partial\psi}{\partial t} - \frac{2\gamma}{r} \psi \quad \dots\dots(5.51),$$

where

$$\nabla_1^2\psi \equiv \frac{\partial^2\psi}{\partial z^2} + \frac{\partial^2\psi}{\partial R^2} + \frac{\partial\psi}{R\partial R} + \frac{\partial^2\psi}{R^2\partial\phi_1^2}.$$

Equation (5.51) has the same form as the wave equation (5.03) in the absence of a magnetic field. Hence the wave function has the form

$$\exp(\pm i\mu\phi_1 - 2\pi i\nu t) \cdot f(r, \theta) = \exp(\pm i\mu\phi \pm i\mu\omega t - 2\pi i\nu t) \cdot f(r, \theta),$$

and the frequencies are now given by the expression

$$\nu \pm \mu\omega/2\pi = (N/n^2) \pm (\mu\omega/2\pi),$$

where  $\mu$  is, of course, either an integer or zero.

## §6. THE EMISSION OF RADIATION

In this section the transitions by which an atom passes from one energy level to another will be studied. The principal results which will be obtained are the following:

- a. The classical "selection rules" of spectral theory.
- b. The emission of radiation in quanta.
- c. The intensities of spectral lines.

These results are all reached by working with a wave equation modified to allow for the reaction of the radiation on the atom.

Although there may be several stationary states associated with each energy level the discussion will be limited for the sake of simplicity to the simplest type of transition, namely transition from one stationary state to another.

The method employed is one of successive approximations. If

$$\psi_1 = u_1 \exp(-\omega_1 t) \text{ and } \psi_2 = u_2 \exp(-\omega_2 t)$$

are the wave functions in the initial and final states, we assume that during the process of transition the wave function has the form

$$\psi = a_1\psi_1 + a_2\psi_2,$$

where  $a_1$  and  $a_2$  are coefficients depending only on the time. Since the process of

transition must be slow compared with the frequency of oscillation of  $\psi_1$  and  $\psi_2$ , we ignore the variation of  $a_1$  and  $a_2$  with the time in calculating the instantaneous values of the charge and current density carried by the wave. From these values we calculate the electromagnetic potentials of the field of radiation emitted and hence the rate of emission of energy. We then return to the wave equation and introduce a correcting term to allow for the reaction of the radiation on the waves. We can then determine the rates of change of  $a_1$  and  $a_2$  and thus estimate the probability of a transition.

### 6.1. The Electromagnetic Potentials.

If we write  
and  $\sigma_{kn} = (he/4\pi mc) (u_k^* \text{grad } u_n - u_n \text{grad } u_k^*)$  .....(6.11),  
the instantaneous values of the charge and current density are

$$\rho = \sum a_k^* a_n \rho_{kn} \exp \omega_{kn} t \quad \text{.....(6.12),}$$

and  $\sigma = \sum a_k^* a_n \sigma_{kn} \exp \omega_{kn} t$  .....(6.13).  
where  $\omega_{kn} = 2\pi\nu(\nu_k - \nu_n)$

When we are considering the values of these quantities at the point whose position vector is  $\mathbf{r}'$ , this fact will be indicated by attaching primes to the corresponding symbols.

The values of the scalar and vector potentials due to the charge and current carried by the waves are calculated at the point whose position vector is  $\mathbf{r}$ , and they are given by the equations

$$V = \sum a_k^* a_n V_{kn}, \quad \mathbf{A} = \sum a_k^* a_n \mathbf{A}_{kn} \quad \text{.....(6.14),}$$

$$V_{kn} = \int \exp \omega_{kn} (t - R/c) \cdot \rho'_{kn}/R \cdot d\tau' \quad \text{.....(6.15),}$$

$$\mathbf{A}_{kn} = \int \exp \omega_{kn} (t - R/c) \cdot \sigma'_{kn}/R \cdot d\tau'$$

where

$$R = |\mathbf{r} - \mathbf{r}'|$$

$$= r \{1 - 2(\mathbf{r} \cdot \mathbf{r}')/r^2 + (r'/r)^2\}^{1/2} \quad \text{.....(6.16).}$$

Since the "partial potentials"  $V_{kn}$  and  $\mathbf{A}_{kn}$  are the only functions which involve the factor  $\exp \omega_{kn} t$ , they must separately satisfy the equation

$$c \operatorname{div} \mathbf{A}_{kn} + \partial V_{kn}/\partial t = 0.$$

Hence if we define the vector  $\mathbf{s}_{kn}$  by the equation

$$\omega_{kn} \mathbf{s}_{kn} = c \int \exp \omega_{kn} (t - R/c) \cdot \sigma'_{kn}/R \cdot d\tau' \quad \text{.....(6.17),}$$

we may write

$$c\mathbf{A} = \partial \mathbf{s}/\partial t, \quad V = -\operatorname{div} \mathbf{s} \quad \text{.....(6.18).}$$

where

$$\mathbf{s} = \sum a_k^* a_n \mathbf{s}_{kn}$$

It may now be verified that the magnetic and electric intensities are

$$\mathbf{H} = c^{-1} \operatorname{curl} \dot{\mathbf{s}}, \quad \mathbf{E} = \operatorname{curl} \operatorname{curl} \mathbf{s} \quad \text{.....(6.19).}$$

### 6.2. Dipole Radiation.

It was shown in § 5.3 that the greater part of the charge and current are confined to the interior of a sphere of radius  $a_n$  with its centre at the nucleus,  $a_n$  being the radius of the corresponding orbit in Bohr's theory. Now

$$2h\nu_n = e^2/a_n \quad \text{.....(6.21).}$$

Hence  $|\omega_{kn}a_n/c| < 2\pi\nu_n a_n/c = \pi e^2/hc = 0.0036$  (dimensionless) (6.22),

and  $|\omega_{kn}| \cdot (\mathbf{r}\mathbf{r}') (rc)^{-1}$  is of the same order when  $r' \approx a_n$ . Therefore if  $r$  is chosen to be large compared with  $a_n$ , we may replace  $R^{-1} \exp \omega_{kn} (t - R/c)$  by  $r^{-1} \exp \omega_{kn} (t - r/c)$  in equations (6.15) and (6.17), and limit the range of integration to the interior of the sphere  $r' = 10a_n$  (say), thus obtaining

$$r\omega_{kn} \mathbf{s}_{kn} = c \exp \omega_{kn} (t - r/c) \cdot \int \boldsymbol{\sigma}'_{kn} d\tau' \quad \dots (6.23).$$

It is really immaterial whether the range of integration is thus restricted or not. If we include all space in the range we may transform the integral as in equations (3.21), (3.22). In virtue of the wave-equation (5.03) and the definitions of (6.11) we find that

$$c \operatorname{div} \boldsymbol{\sigma}_{kn} + \omega_{kn} \rho_{kn} = 0 \quad \dots (6.24).$$

Now define the polarisation  $\mathbf{p}_{kn}$  by the integral

$$\mathbf{p}_{kn} = \int \mathbf{r}' \rho'_{kn} d\tau' = \mathbf{p}^*_{nk}, \quad \dots (6.25),$$

then  $c \int \boldsymbol{\sigma}'_{kn} d\tau' = -c \int \mathbf{r}' \operatorname{div} \boldsymbol{\sigma}'_{kn} d\tau = \omega_{kn} \int \mathbf{r}' \rho'_{kn} d\tau' = \omega_{kn} \mathbf{p}_{kn} \dots (6.26).$

Hence  $\mathbf{s}_{kn} = \mathbf{p}_{kn} r^{-1} \exp \omega_{kn} (t - r/c) \dots (6.27).$

By referring to equation (6.18) it will now be seen that at great distances from the nucleus the field produced by the waves consists of a steady electrostatic field superimposed on an oscillating field of the type due to a Hertzian doublet or dipole of strength

$$\mathbf{p}_{12} \exp \omega_{12} t + \mathbf{p}_{21} \exp \omega_{21} t \quad \dots (6.28).$$

### 6.3. The Selection Rules.

In spherical polar coordinates  $(r, \theta, \phi)$  we have

$$\mathbf{p}_{12} = -e \int_0^\infty r^2 dr \int_0^\pi \sin \theta d\theta \int_0^{2\pi} r u_1^* u_2 d\phi$$

(dropping the primes in the integral). Let

$$u_1 \exp (-2\pi i \nu_1 t) = \psi(\lambda_1, \mu_1, \nu_1),$$

$$u_2 \exp (-2\pi i \nu_2 t) = \psi(\lambda_2, \mu_2, \nu_2),$$

in the notation of equation (5.21).

The following results may easily be verified:

I. If  $\mu_1 = \mu_2$ ,  $\mathbf{p}_{12}$  is parallel to the  $z$ -axis.

II. If  $\mu_1 - \mu_2 = \pm 1$ ,  $\mathbf{p}_{12}$  is perpendicular to the  $z$ -axis.

III. If none of these relations is satisfied,  $\mathbf{p}_{12} = 0$ .

These results constitute the equatorial selection principle. By employing well-known results in harmonic analysis it may be shown that

IV. If  $\lambda_1 - \lambda_2 \neq \pm 1$ ,  $\mathbf{p}_{12} = 0$ .

This is the azimuthal selection principle.

If the polarisation  $\mathbf{p}_{12}$  vanishes, it is evident that the transition does not give rise to any radiation, for the strength of the equivalent Hertzian doublet is zero (6.28).

It also follows from the form of the integral for  $\mathbf{p}_{12}$  that this quantity is wholly real. Henceforward let us write for the sake of brevity

$$\mathbf{p}_{12} = \mathbf{p} \text{ and } \omega = -i\omega_{12} = 2\pi(\nu_1 - \nu_2) \quad \dots (6.31).$$



6.4. *The Rate of Emission of Energy.*

It follows from equations (6.19) and (6.27) that the magnetic intensity of the radiation field is

$$\mathbf{H} = (\omega/c)^2 \text{grad } \mathbf{r} \wedge (a_1^* a_2 \mathbf{s}_{12} + a_2^* a_1 \mathbf{s}_{21}).$$

Hence if the axes be chosen so that the polarisation  $\mathbf{p}$  is directed along the  $z$ -axis,

$$\begin{aligned} H^2 &= \frac{\omega^4 p^2 \sin^2 \theta}{r^2 c^4} \{a_1^* a_2 \exp \omega_{12}(t - r/c) + a_2^* a_1 \exp \omega_{21}(t - r/c)\}^2 \\ &= \frac{4\omega^4 a_1 a_2 a_1^* a_2^* p^2}{r^2 c^4} \sin^2 \theta \cdot \cos^2 \omega(t - r/c - \alpha), \end{aligned}$$

where  $\alpha$  is the argument of  $a_1^* a_2$ .

Since the radiation is due to a Hertzian doublet, the electric and magnetic intensities are equal in magnitude and perpendicular in direction when  $r$  is large. Therefore the rate at which energy crosses a large sphere of radius  $B$  is

$$\begin{aligned} &\int_0^\pi (c/4\pi) [\mathbf{E} \wedge \mathbf{H}]_B \cdot 2\pi B^2 \sin \theta d\theta \\ &= \frac{1}{2} c \int_0^\pi H^2_B \cdot B^2 \sin \theta d\theta \\ &= \frac{8\omega^4 a_1 a_2 a_1^* a_2^* p^2}{3c^3} \cos^2 \omega(t - B/c - \alpha) \quad \dots\dots(6.41)^\dagger. \end{aligned}$$

6.5. *The Modified Wave Equation.*

Fermi<sup>†</sup> modified the wave equation by introducing an extra term into the electrostatic potential  $V$  to represent the reaction of the radiation. But, since a field of radiation always requires the electromagnetic vector potential for its specification, it seems better to proceed as follows.

An electron moving with an acceleration  $\alpha$  radiates energy at the rate  $2e^2 \alpha^2 / 3c^3$  ergs per second and experiences a retarding force of  $2e^2 \dot{\alpha} / 3c^3$  dynes. This is the force which would arise from a vector potential

$$\mathbf{A} = (2e/3c^2) \cdot \alpha.$$

Now it has been shown (§ 6.4 that the atom radiates energy at the rate  $2\omega^4 \beta^2 / 3c^3$  where

$$\beta = a_1^* a_2 \mathbf{p} \exp \omega_{12}(t - B/c) + a_2^* a_1 \mathbf{p} \exp \omega_{21}(t - B/c) \quad \dots\dots(6.51).$$

Hence we shall modify the wave equation by introducing the vector potential

$$\mathbf{A} = (2\omega^2 / 3c^2) \beta \quad \dots\dots(6.52).$$

The wave equation now becomes

$$L(\psi) \equiv \frac{\partial \psi}{\partial t} + \frac{h}{4\pi m_e} \nabla^2 \psi - \frac{2\pi e}{h} V_0 \psi + \frac{e}{mc} (\mathbf{A}_0 \cdot \text{grad } \psi) = -\frac{e}{mc} (\mathbf{A} \cdot \text{grad } \psi),$$

$V_0$  and  $\mathbf{A}_0$  being potentials of the nucleus and any external field applied to the atom. If in this equation we substitute

$$\psi = a_1 \psi_1 + a_2 \psi_2,$$

where  $\psi_1$  and  $\psi_2$  satisfy  $L(\psi) = 0$ , we find that

$$\dot{a}_1 \psi_1 + \dot{a}_2 \psi_2 = -(e/mc) \cdot (\mathbf{A} \cdot a_1 \text{grad } \psi_1 + a_2 \text{grad } \psi_2) \quad \dots\dots(6.53).$$

<sup>†</sup> M. Bohr and P. Jordan, "Zur Quantenmechanik," *Zeits. f. Physik*, 34, 858-88 (1925).

<sup>†</sup> E. Fermi, "Sul meccanismo dell'emissione nel meccanismo ondulatorio," *Accad. Lincei* (6), 5, 795-800 (1927).

### 6.6. Dirac's Equations.

We now obtain the differential equations for  $a_1$  and  $a_2$  in the form given by Dirac†. Multiply equation (6.53) by  $\psi_k^*$  and integrate over all space. If we write

$$a_{kn} = -(e/mc) \int (\mathbf{A} \cdot \psi_k^* \text{grad } \psi_n) d\tau \quad \dots\dots(6.61),$$

we find that

$$\dot{a}_1 \int \psi_k^* \psi_1 d\tau + \dot{a}_2 \int \psi_k^* \psi_2 d\tau = a_{k1} a_1 + a_{k2} a_2 \quad \dots\dots(6.62).$$

Since the total charge carried by the waves remains constantly equal to  $-e$ , we deduce that

$$\int (a_1^* a_2 \psi_1^* \psi_2 + a_1^* a_2 \psi_1^* \psi_2 + a_2^* a_1 \psi_2^* \psi_1 + a_2^* a_2 \psi_2^* \psi_2) d\tau = 1.$$

If, for convenience, we assume the functions  $\psi_1, \psi_2$ , normalised so that

$$\int \psi_1^* \psi_2 d\tau = 1 = \int \psi_2^* \psi_1 d\tau,$$

we may conclude that

$$a_1^* a_1 + a_2^* a_2 = 1 \quad \dots\dots(6.63),$$

and

$$\int \psi_1^* \psi_2 d\tau = 0 = \int \psi_2^* \psi_1 d\tau.$$

Hence equations (6.62) become

$$\begin{aligned} \dot{a}_1 &= a_{11} a_1 + a_{12} a_2 \\ \dot{a}_2 &= a_{21} a_1 + a_{22} a_2 \end{aligned} \quad \dots\dots(6.64).$$

These are Dirac's equations. Now from equation (6.61)

$$a_{nk}^* = -(e/mc) \int (\mathbf{A} \cdot \psi_n \text{grad } \psi_k^*) d\tau,$$

and

$$a_{kn} + a_{kn}^* = -(e/mc) \int \text{div} (\mathbf{A} \psi_k^* \psi_n) d\tau = 0,$$

since  $\psi_n$  contains a factor  $\exp(-kr)$ . Therefore

$$\begin{aligned} a_{kn} &= \frac{1}{2} (a_{kn} - a_{nk}^*) \\ &= (2\pi i / h) \exp \omega_{kn} t \cdot \int (\mathbf{A} \cdot \boldsymbol{\sigma}_{kn}) d\tau \\ &= (2\pi \omega_{kn} / hc) \exp \omega_{kn} t (\mathbf{A} \cdot \mathbf{p}_{kn}) \end{aligned} \quad \dots\dots(6.65),$$

from (6.26).

### 6.7. The Emission of Quanta.

Since it is only the secular charges in  $a_1$  and  $a_2$  which will be revealed in experiment, only the constant coefficients on the right-hand side of equations (6.64) will be retained, the periodic terms being neglected. On introducing the values of  $a_{kn}$  and  $\mathbf{A}$  from (6.65), (6.51) and (6.52), we obtain Fermi's equations

$$\dot{a}_1 = -A a_1 a_2^* a_2, \quad \dot{a}_2 = +A a_1^* a_1 a_2,$$

where

$$A = 4\pi \omega^3 p^2 / 3hc^3 \quad \dots\dots(6.71).$$

Hence

$$d(a_1^* a_1) / dt = -2A a_1 a_2 a_1^* a_2^* \quad \dots\dots(6.72)$$

and

$$\int_{-\infty}^{\infty} a_1 a_2 a_1^* a_2^* dt = -(2A)^{-1} [a_1^* a_2]_{-\infty}^{\infty}.$$

But in a transition ( $\nu_1 \rightarrow \nu_2$ ) the quantity  $a_1^* a_1$ , passes from unity to zero (6.63). Therefore

$$\int_{-\infty}^{\infty} a_1 a_2 a_1^* a_2^* dt = (2A)^{-1} \quad \dots\dots(6.73).$$

† P. A. M. Dirac, "On the Theory of Quantum Mechanics," *Proc. R. S. A.*, 112, 661-77 (1926).

The total amount of energy radiated during the transition is

$$E_{12} = \frac{8\omega^4 p^2}{3c^3} \int_{-\infty}^{\infty} a_1 a_2 a_1^* a_2^* \cos^2 \omega (t - B/c - \alpha) dt,$$

from (6.41). Since the integral is the product of a rapidly fluctuating periodic term and a slowly varying term, we may replace the former by its mean value, which is one-half. We then find from (6.71) and (6.73) that

$$E_{12} = 2\omega^4 p^2 / 3c^3 A = h(\nu_1 - \nu_2) \quad \dots\dots(6.74).$$

It follows from (6.71) and (6.31) that if

$$0 > \nu_1 > \nu_2,$$

$A$  and  $\omega$  are positive, and that the transition is accompanied by the emission of a quantum of radiation of frequency  $\nu = \nu_1 - \nu_2$ .

### 6.8. The Intensities of Spectral Lines.

It follows from equations (6.63) and (6.72) that

$$a_1^* a_1 = \{1 + \exp 2A(t - t_0)\}^{-1}, \quad a_2^* a_2 = \exp 2A(t - t_0) \{1 + \exp 2A(t - t_0)\}^{-1},$$

while

$$a_1^* a_1 a_2^* a_2 = \frac{1}{4} \operatorname{sech}^2 A(t - t_0),$$

$t_0$  being the time at which the transition is half completed. Hence from (6.41) the maximum mean rate of emission of energy is

$$\omega^4 p^2 / 3c^3.$$

It is accordingly usual to assume that the intensity of the spectral line of frequency  $\nu_{kn}$  emitted by the atom is proportional to  $\nu_{kn}^4 p_{kn}^2$  where  $p_{kn}$  is the polarisation for the transition ( $\nu_k \rightarrow \nu_n$ ).

If  $A_{kn}$  is the "probability" of a transition, the rate of emission of energy from  $M$  atoms would be  $MA_{kn}h\nu_{kn}$ , since one quantum is emitted in each transition. Therefore the coefficient of emission,  $A_{kn}$ , is proportional to  $\nu_{kn}^3 p_{kn}^2$ .

## §7. THE PRINCIPLES OF RELATIVISTIC WAVE MECHANICS

In this section the principles of relativistic wave mechanics of unpolarised waves will be developed briefly, the discussion following a course parallel to the investigations of §§ 2 and 3. By way of illustration a simple theory of the Compton effect will be added.

### 7.1. Construction of the Wave Equation.

Consider the motion of an electron, of charge  $-e$  and proper mass  $m$ , moving with velocity  $\mathbf{v}$  in an electromagnetic field with scalar and vector potentials  $V$  and  $\mathbf{A}$ . The Lagrangian function is

$$\Lambda = -mc^2(1 - v^2/c^2)^{\frac{1}{2}} + eV - (\mathbf{A} \cdot \mathbf{v})(e/c),$$

the momentum is  $\mathbf{p} = \partial\Lambda/\partial\mathbf{v} = m\mathbf{v}(1 - v^2/c^2)^{-\frac{1}{2}} - e\mathbf{A}/c,$

and the total energy of the electron is

$$W = (\mathbf{p} \cdot \mathbf{v}) - \Lambda = mc^2(1 - v^2/c^2)^{-\frac{1}{2}} - eV.$$

Hence the total energy and the components of momentum are connected by the relation (compare equation (2.16))

$$m^2c^2 + (\mathbf{p} + e\mathbf{A}/c)^2 = (W + eV)^2/c^2.$$

As in § 2, we multiply this equation through by the wave function  $\psi$  and then replace  $\mathbf{p}\psi$  by  $(\hbar/2\pi i) \nabla\psi$ , and  $W\psi$  by  $(-\hbar\partial\psi/2\pi i\partial t)$  (equations (2.11) and (2.12)), thus obtaining as one general wave equation

$$\left(\frac{e}{c}\mathbf{A} + \frac{\hbar}{2\pi i}\nabla\right)^2\psi + m^2c^2\psi = \left(eV - \frac{\hbar}{2\pi i}\frac{\partial}{\partial t}\right)^2\psi/c^2 \quad \text{.....(7.11).}$$

On making use of the relation

$$c \operatorname{div} \mathbf{A} + \partial V/\partial t = 0,$$

this reduces to

$$\begin{aligned} \nabla^2\psi - \partial^2\psi/c^2\partial t^2 &= (2\pi mc/\hbar)^2\psi + (2\pi e/\hbar c)^2(A^2 - V^2)\psi \\ &\quad - (4\pi e/\hbar c)\{(\mathbf{A} \cdot \operatorname{grad} \psi) + (V\partial\psi/c\partial t)\} \quad \text{.....(7.12).} \end{aligned}$$

The accurate relation between the wave-length  $\lambda = \hbar/\rho$ , and the frequency  $\nu = W/\hbar$  for free electric waves is derived from the relation

$$m^2c^2 + p^2 = W^2/c^2,$$

which yields

$$\lambda^2(\nu^2 - \nu_0^2) = c^2 \quad \text{.....(7.13),}$$

where  $\nu_0 = mc^2/\hbar$  is the "threshold frequency" which forms a natural lower limit to the possible frequencies of free electric waves.

## 7.2. Lagrangian Form of the Wave Equation†.

As in § 2 we write

$$\psi = \exp(2\pi i s/\hbar) \text{ and } \psi^* = \exp(-2\pi i s^*/\hbar),$$

and retain the same Lagrangian function,  $L_0$  (2.26), for the electromagnetic field. We find that the wave equation (7.12) may be deduced from the Lagrangian function  $L$ , where

$$L/\psi^*\psi = m^2c^2 + (\operatorname{grad} s + e\mathbf{A}/c)(\operatorname{grad} s^* + e\mathbf{A}/c) - (eV - \dot{s})(eV - \dot{s}^*)/c^2 \quad (7.21).$$

To interpret this function, let

$$\rho = -\partial L/\partial V = -\frac{\hbar e}{2\pi i c^2} \left( \psi^* \frac{\partial \psi}{\partial t} - \psi \frac{\partial \psi^*}{\partial t} \right) + \frac{2e^2}{c^2} \psi^* \psi V \quad \text{.....(7.22),}$$

and

$$\boldsymbol{\sigma} = \partial L/\partial \mathbf{A} = \frac{\hbar e}{2\pi i c} (\psi^* \operatorname{grad} \psi - \psi \operatorname{grad} \psi^*) + \frac{2e^2}{c^2} \psi^* \psi \mathbf{A} \quad \text{.....(7.23),}$$

then  $L$  may be rewritten as

$$\begin{aligned} m^2c^2\psi^*\psi + (\hbar^2/4\pi^2) \left( \operatorname{grad} \psi \cdot \operatorname{grad} \psi^* - \frac{\partial \psi}{\partial t} \cdot \frac{\partial \psi^*}{\partial t} \right) - (A^2 - V^2)e^2\psi^*\psi/c^2 \\ + (\mathbf{A} \cdot \boldsymbol{\sigma}) - V\rho \quad \text{.....(7.24).} \end{aligned}$$

As in § 2, if we vary  $V$  and  $\mathbf{A}$  in the complete Lagrangian function  $L_0 + L$ , we obtain Maxwell's equations

$$\operatorname{div} \mathbf{E} = 4\pi\rho \text{ and } \operatorname{curl} \mathbf{H} - \partial \mathbf{E}/\partial t = 4\pi\boldsymbol{\sigma}.$$

† W. Gordon, "Der Comptoneffekt nach der Schrödingerschen Theorie," *Zeits. f. Physik*, **40**, 117-33 (1926).

Hence  $\rho$  is the volume density of the charge carried by the waves while  $\sigma$  is the current density; and from these relations the equation of continuity

$$c \operatorname{div} \sigma + \partial \rho / \partial t = 0 \quad \dots\dots(7.25)$$

follows at once. It will now be evident which parts of the total action density  $L$  are to be attributed to the electric waves and which part to their interaction with the electromagnetic field.

### 7.3. *The Relativistic Form of Madelung's Equation.*

It will now be shown that to a first approximation the motion of electric charge determined by the wave equation (7.12) agrees with the predictions of the relativistic electron theory. As in § 3.1 we write

$$\psi = \alpha \exp(2\pi i \beta / h) \quad \dots\dots(7.31),$$

where  $\alpha$  and  $\beta$  are both real quantities. Then we find from equations (7.22) and (7.23) that

$$\rho = -(2e\alpha^2 c^{-2}) (\partial \beta / \partial t - eV) \quad \dots\dots(7.32),$$

and

$$\sigma = (2e\alpha^2 c^{-1}) (\operatorname{grad} \beta + e\mathbf{A}/c) \quad \dots\dots(7.33).$$

The wave equation is now equivalent to the equation of conservation (7.25) and the generalisation of Madelung's equation, namely

$$4e^2 m^2 + (\sigma^2 - \rho^2) \alpha^{-4} = (h^2 e^2 / \pi^2 c^2 \alpha) (\nabla^2 \alpha - \ddot{\alpha} / c^2) \quad \dots\dots(7.34).$$

If this equation be rewritten in the form

$$m^2 c^2 + (\operatorname{grad} \beta + e\mathbf{A}/c)^2 - (\partial \beta / \partial t - eV)^2 c^{-2} = (h^2 / 4\pi^2 \alpha) (\nabla^2 \alpha - \ddot{\alpha} / c^2) \quad \dots\dots(7.35),$$

it will be recognised as the Hamiltonian equation for an electron whose internal energy is not  $mc^2$  but  $mc^2 - (h^2 / 4\pi^2 m \alpha) (\nabla^2 \alpha - \ddot{\alpha} / c^2)$ .

Since the additional term is in general small we see that  $\beta$  is, approximately, the "action-function" for an electron.

Hence, according to the principles of classical relativity, a system of electrons projected into an electromagnetic field of potentials  $V$  and  $\mathbf{A}$  would move so that at any point their velocity  $\mathbf{v}$  was given by the equations

$$m\mathbf{v} (1 - v^2/c^2)^{-\frac{1}{2}} = \operatorname{grad} \beta + e\mathbf{A}/c,$$

$$mc^2 (1 - v^2/c^2)^{-\frac{1}{2}} = \partial \beta / \partial t - eV,$$

whence

$$\mathbf{v} = c\sigma/\rho.$$

Therefore the velocity which the electrons would have at any point agrees with the velocity with which the electric charge is carried by the waves.

### 7.4. *The Compton Effect\*.*

Only the wave-length of the scattered light and not its intensity will be determined here. The method adopted may be outlined as follows: (a) An atmosphere of electrons under the action of an incident beam of light is considered. (b) The

\* P. A. M. Dirac, "The Compton Effect in Wave Mechanics," *Proc. Camb. Phys. Soc.* 23, 500-7 (1926); "The Relativity Quantum Mechanics with an Application to Compton Scattering," *Proc. R. S. A.*, 111, 405-23 (1926); W. Gordon, *loc. cit.*, *supra*; E. Schrödinger, "Über den Comptoneffekt," *Ann. d. Phys.* 82, 257-64 (1927).

complete wave function for a system of free electrons may be built up from elementary wave functions each of which is associated with electrons of the same energy and momentum. (c) The small changes which are produced in these elementary wave functions by the incident beam are determined, and then (d) the changes in the charge and current carried by the waves are calculated. (e) From these results the wave-length of the radiation emitted in any chosen direction can then be determined.

(a) Let the incident light have frequency  $\nu_1$ , and wave-length  $\lambda_1$ , and let its direction of propagation be given by the unit vector  $\mathbf{n}_1$ . If we write

$$\begin{aligned} E_1 &= h\nu_1, \quad \mathbf{f}_1 = h\mathbf{n}_1/\lambda_1, \\ h\phi_1 &= 2\pi \{(\mathbf{f}_1 \cdot \mathbf{r}) - E_1 t\} \end{aligned} \quad \text{.....(7.41),}$$

we may take the scalar and vector potentials of the incident beam to be

$$V = 0, \quad \mathbf{A} = \mathbf{a} \cos \phi_1 \quad \text{.....(7.42).}$$

(b) A system of electrons all of energy  $W_n$  and momentum  $\mathbf{p}_n$  is replaced in our wave mechanics by a wave function

$$\psi_n = \alpha_n \exp(2\pi i/h) \{(\mathbf{p}_n \cdot \mathbf{r}) - W_n t\} \quad \text{.....(7.43),}$$

where

$$m^2 c^2 + p_n^2 = W_n^2/c^2.$$

(c) We now rewrite the wave equation (7.12) introducing the values of  $V$  and  $\mathbf{A}$  from (7.41) and (7.42) but neglecting the terms in  $a^2$ . We thus obtain

$$\nabla^2 \psi - \partial^2 \psi / c^2 \partial t^2 - (2\pi m c / h)^2 \psi = - (4\pi e / h c) \cdot \cos \phi_1 (\mathbf{a} \cdot \text{grad } \psi) \quad \text{.....(7.44).}$$

In the right-hand side of this equation we substitute, as a first approximation, the value of  $\psi$  (7.43) for the undisturbed wave system. Then

$$\nabla^2 \psi - \partial^2 \psi / c^2 \partial t^2 - (2\pi m c / h)^2 \psi = (8\pi^2 e / h^2 c) (\mathbf{a} \cdot \mathbf{p}_n) \psi_n \cos \phi_1.$$

The solution of this equation is

$$\psi = \psi_n (1 - 2i\delta \sin \phi_1) \quad \text{.....(7.45),}$$

where  $\delta$  is a constant, depending on  $\mathbf{a}$ .

(d) The complete wave function therefore will consist of the sum or integral of a number of terms of the form

$$\alpha_n \{ \exp i s_n - \delta \exp i (s_n + \phi_1) + \delta \exp i (s_n - \phi_1) \},$$

where

$$h s_n = 2\pi \{(\mathbf{r} \cdot \mathbf{p}_n) - W_n t\}.$$

When the charge and current density are calculated by means of equations (7.32) and (7.33) the resulting expressions may each be divided into three parts.

(i) The first part contains terms independent of  $\delta$  and gives the original charge and current due to the free electrons.

(ii) The second part contains terms involving  $\delta$  linearly, and involves the coordinates  $\mathbf{r}$  and  $t$  only in terms of the form

$$f_{mn}(t) = \cos(s_m - s_n \pm \phi_1).$$

(iii) The third part contains terms involving  $\delta^2$  and will therefore be neglected.

(e) The radiation emitted is determined as in equations (6.15) by expressing the potentials for the scattered light as integrals of the form

$$\int f_{mn}(t - R/c) \cdot d\tau'/R,$$

where  $R = |\mathbf{r}\mathbf{n}_2 - \mathbf{r}'| = r\{1 - 2(\mathbf{r}' \cdot \mathbf{n}_2)r^{-1} + (\mathbf{r}'/r)^2\}^{\frac{1}{2}},$

and  $\mathbf{n}_2$  is a unit vector giving the direction of scattering considered. When we consider the scattered radiation at a great distance from the scattering system we may write

$$R \doteq r - (\mathbf{r}' \cdot \mathbf{n}_2),$$

but since the scattering system is no longer of atomic dimensions as in § 6.2 we must not make the approximation  $R \doteq r$ . The argument of  $f_{mn}$  may now be written as

$$(2\pi/h)\{\mathbf{r}' \cdot \mathbf{p}_m - \mathbf{p}_n \pm \mathbf{f}_1\} - (2\pi/h)\{W_m - W_n \pm E_1\}(t - r/c) \\ - (2\pi/h)(W_m - W_n \pm E_1)(\mathbf{r}' \cdot \mathbf{n}_2)/c.$$

The integrals involving  $f_{mn}$  evidently represent a radiation of frequency

$$\nu_2 = (E_1 \mp W_m \pm W_n)/h.$$

If we write  $E_2 = h\nu_2$ ,  $\mathbf{f}_2 = h\mathbf{n}_2/\lambda_2$ ,  $\lambda_2 = c/\nu_2$  .....(7.46),  
the argument of  $f_{mn}$  becomes

$$(2\pi/h)\{\mathbf{r}' \cdot \mathbf{p}_m - \mathbf{p}_n \pm \mathbf{f}_1 \mp \mathbf{f}_2\} \pm (2\pi\nu_2)(t - r/c).$$

Hence the mean value of  $f_{mn}$  taken over the whole of the scattering system will be zero unless

$$\mathbf{p}_m - \mathbf{p}_n = \pm (\mathbf{f}_2 - \mathbf{f}_1) \quad \text{.....(7.47).}$$

This equation, together with

$$W_m - W_n = \pm (E_2 - E_1) \quad \text{.....(7.48),}$$

determines the frequency of the light scattered in the direction defined by  $\mathbf{n}_2$ .

But these are precisely the equations which express Compton's original theory of this phenomenon. Take the upper sign and write  $m = 1$ ,  $n = 2$ . Then equation (7.47) equates the loss in the momentum of a quantum,  $\mathbf{f}_1 - \mathbf{f}_2$ , to the gain in the momentum of a scattering electron,  $\mathbf{p}_2 - \mathbf{p}_1$ . Equation (7.48) equates the loss in the energy of the quantum,  $E_1 - E_2$ , to the gain in the energy of the scattering electron,  $W_2 - W_1$ . Hence the wave-length of the scattered light determined by wave mechanics must agree with that determined by Compton's theory.

## DISCUSSION

THE PRESIDENT: I must congratulate the author on his manner of presenting a very difficult subject and thank him for the new angles of view which he has shown us.

# THE EFFECT OF SUPERIMPOSED MAGNETIC FIELDS ON DIELECTRIC LOSSES AND ELECTRIC BREAKDOWN STRENGTH

BY ALLAN MONKHOUSE, M.I.E.E., A.M.I.MECH.E.

*Received October 4, 1928. Read in title November 23, 1928*

**ABSTRACT.** A description is given of tests made to determine the effect of superimposed magnetic fields on the insulating properties of dielectrics. As a result of the tests made the author reaches the conclusion that both the electric strength of dielectrics and the dielectric losses in the same are seriously affected by the presence of superimposed magnetic fields. A theoretical explanation of the phenomena is suggested by a paper read by Professor A. Smouloff before the Mathematical Conference at Bologna in September 1928. The investigation is not complete and the author is proceeding with dielectric loss measurements using more refined laboratory apparatus than that which he had available for the series of tests described.

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**D**URING the operation of plant on three extensive 115,000 volt networks involving some 300 miles of transmission lines and heavy generating and transforming plant a number of phenomena were observed in connection with insulation failures and corona discharges which did not yield to ready explanation, and consequently the idea was suggested by the author's colleague, Mr L. C. Thornton, that dielectrics when simultaneously subjected to a magnetic field superimposed on a dielectric field had their insulating characteristics appreciably affected by the presence of the magnetic field.

A search through the available literature on the subject of dielectrics yielded no experimental evidence of such phenomena having been previously observed or discussed in relation to solid dielectrics. The effect of the presence of a magnetic field on the electric strength of various gaseous dielectrics has however been investigated by numerous authorities. From these investigators' experiments the fact seemed to have been established that the presence of a magnetic field tends to increase slightly the sparking or breakdown voltage of gaseous dielectrics under most practical conditions.

In order to make a preliminary test to investigate this phenomenon the apparatus shown in Fig. 1 was set up. This apparatus consisted of a B.E.S.A. Standard insulating oil test cup with one electrode extended so that it constituted the core of an electromagnet. A large number of tests were made on different oils using both A.C. and D.C. magnetic fields. In the case of alternating current the phase relationship of the dielectric field to the magnetic field was not observable but calculation showed that there was approximately no phase difference between these fields. The results obtained are tabulated in Table I.



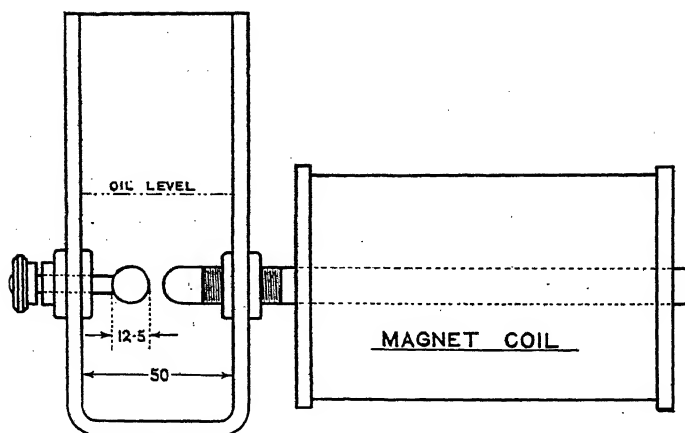


Fig. 1. Apparatus for preliminary investigation.

Table I: Breakdown voltage.

*Current: 50  $\times$  A.C. at 15.5° C.*

	1ST SERIES			2ND SERIES	
	Without magnetic field	With A.C. magnetic field 1.1 amps excitation	With A.C. magnetic field 2.0 amps excitation	Without magnetic field	With D.C. magnetic field core saturated
No. of tests	10	10	10	10	10
Average breakdown voltage	46222	43111	38888	37875	35500
3RD SERIES					
	Without magnetic field	With A.C. magnetic field 2.0 amps excitation		Without magnetic field	With A.C. magnetic field 2.0 amps excitation
No. 1 oil sample:			No. 3 oil sample:		
No. of tests	10	10	No. of tests	7	7
Av. breakdown volt.	48450	43450	Av. breakdown volt.	31714	30500
No. 2 oil sample:			No. 4 oil sample:		
No. of tests	5	5	No. of tests	6	6
Av. breakdown volt.	48375	41375	Av. breakdown volt.	40750	34666

From the above table it would appear that the influence of the magnetic field was greater in the case of the drier oils, i.e. those which broke down at a higher voltage.

This result led to experiments on an ordinary commercial dielectric of relatively poor insulating characteristics, i.e. pressboard.

The tests on pressboard were made with standard E.R.A. electrodes with the difference that the lower electrode was made of steel and constituted the pole of an electromagnet. In making the tests the voltage was raised to what was known to be approximately the one minute breakdown value for the material under standard conditions at 15.5° C. in air and the average time before breakdown occurred under various magnetic field conditions was recorded. The results of these tests are shown in Table II.

Table II: Breakdown voltage on 3 mm. pressboard.  
(Material of German manufacture).

## 1ST SERIES

Without magnetic field	With 50 $\times$ A.C. magnetic field 2.0 amps excitation
(a) 10000 V—intact 4 min. 12000 V—failed 1.5 min.	10000 V—intact 4 min. 12000 V—failed 15 sec.
(b) 12000 V—intact 2.5 min. 14000 V—failed 15 sec.	12000 V—intact 2.5 min., failed whilst raising volts at 13500 volts
(c) 14000 V—failed 100 sec.	14000 V—failed 20 sec.
(d) 14000 V—failed 15 sec.	14000 V—failed 6 sec.
(e) 14000 V—failed 75 sec.	14000 V—failed 67 sec.

## 2ND SERIES

	10000 volts	15000 volts	Rising 1000 V per 1 sec.
Without magnetic field	2 intact	2 intact	Failed 18000 V
With D.C. magnetic field (full saturation)	2 intact	1.5 failed	
Without magnetic field	2 intact	2 intact	Failed 19500 V
With D.C. magnetic field (full saturation)	2 intact	0.25 failed	

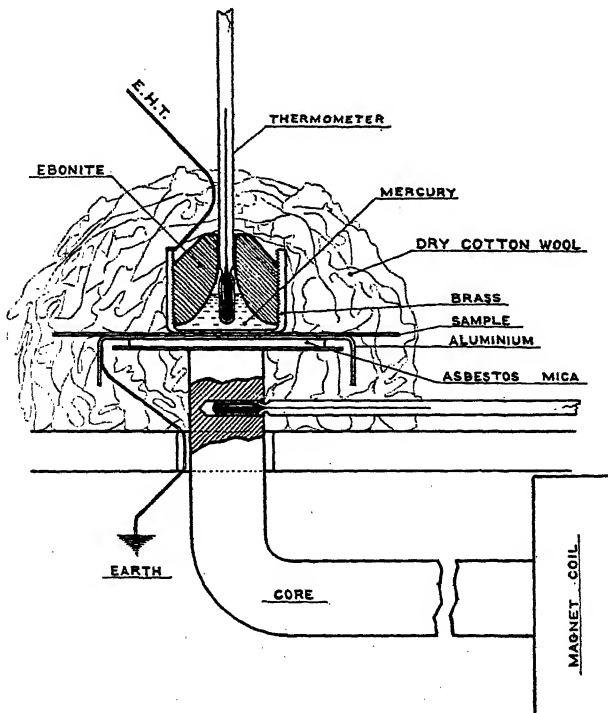


Fig. 2. Apparatus used for results shown in Fig. 3 and Table III.

These results led the author to the view that the magnetic field under certain circumstances had a very marked effect on the dielectric losses in the material and consequently on the ultimate breakdown strength. To check this theory the apparatus shown in Fig. 2 was set up since the conditions and facilities available did not permit of any more accurate method being employed. This test constitutes a modification of the "highest maintained A.C. stress" test described in E.R.A. Report A/S 2\*.

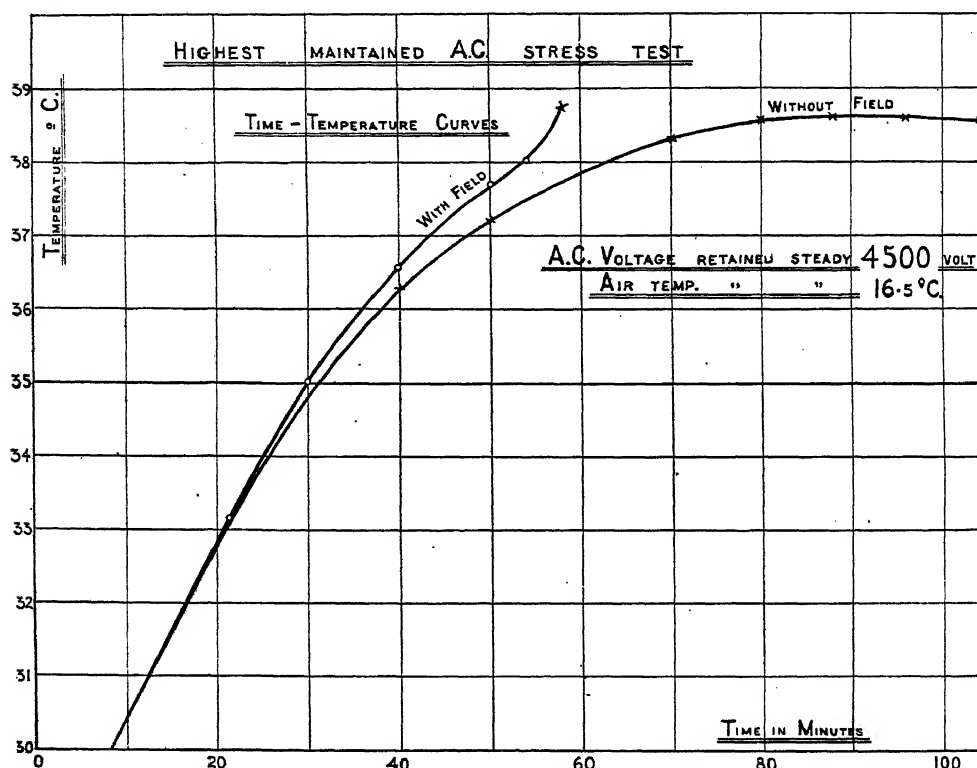


Fig. 3. Tests on varnished cloth.

The material tested was a double thickness of 7 mm. varnished cloth. The curves in Fig. 3 show the average of many tests made. The steep form of the curve, when the magnetic field is superimposed on the dielectric field, suggests a most marked increase of the dielectric loss in the material.

In making this test particular care was taken to isolate the sample from temperature changes due to the heating of the magnet employed. The magnetising coil was arranged at a distance and the temperature of the core was observed and maintained constant.

Following this a number of simple breakdown strength tests (employing standard E.R.A. rules for conditioning and testing) were carried out on samples of varnished cotton cambric. These results are tabulated in Table III.

\* I.E.E. Journal, 60, 794-802 (1922).

Table III

*Time of breakdown in varnished cotton cambric*

## 1ST SERIES. SINGLE THICKNESS

Electrodes standard E.R.A. in form but lower one of aluminium. A.C. voltage of 5500 volts (50  $\sim$ ) was supplied and time of breakdown observed in seconds.

(a)		(b) Same test repeated		(c) Same test repeated	
Without magnetic field	With D.C. magnetic field	Without magnetic field	With D.C. magnetic field	Without magnetic field	With D.C. magnetic field
59	75	65	49	14	6
65	23	52	14	20	15
35	15	13	35	40	16
		35	13	23	42
159	113	33	28	36	32
Av. 53	38	45	25		
		25	30	133	111
		268	194	Av. 26	22
		Av. 38	27		

## 2ND SERIES. DOUBLE THICKNESS

Electrodes standard E.R.A. in form but lower one of aluminium. Voltage applied 10,000 volts.

Without magnetic field	With D.C. magnetic field
124	20
40 (bad crinkled sample)	82
421	37
30	52
115	
730	191
421 (omit as a freak point)	Av. 48
309	
Av. 77	

## 3RD SERIES. DOUBLE THICKNESS

Upper electrode standard E.R.A. in form but lower electrode a copper bar through which 2000 amps A.C. was passed to produce a field round it. Tests recorded on the same line below were made at adjacent places on the sample.

No. 1 MATERIAL (German origin)		No. 2 MATERIAL (Swedish origin)	
Voltage applied 9800 V		Voltage applied 11,300 V	
Time (seconds) to produce failure		Time (seconds) to produce failure	
Without current in electrode	With 2000 amps passing	Without current in electrode	With 2000 amps passing
60	25	350†	60
40	5	20	7
400*	30	40	10
500	60	410	77
Av. 166	20	Av. 137	26

\* No failure.

† No failure. This sample was retested with field on and again produced no failure. Examination showed it to be a sample in which the varnish was thicker than normal.

NOTE. The results in 3rd Series of Table III (although they appear to indicate that the field surrounding a conductor has an effect on the insulation) cannot be regarded as satisfactory. The material employed was not sufficiently homogeneous.

The above described tests seemed to confirm the suggestion that a magnetic field superimposed on a dielectric field increased the dielectric losses and weakened the electric breakdown strength of solid dielectrics and liquid dielectrics (as represented by transformer oil).

A theoretical explanation for the phenomena was suggested by the contents of a paper by Professor A. Smouloff\*. Professor Smouloff's explanation of the mechanism of electric breakdown appeared to be capable of extension to explain the observed phenomena.

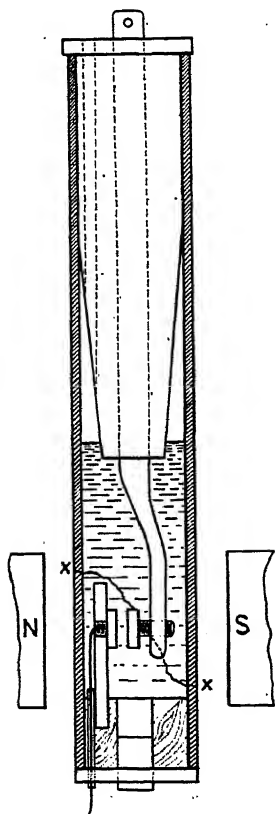


Fig. 4. Abandoned design of apparatus showing fracture x..x.

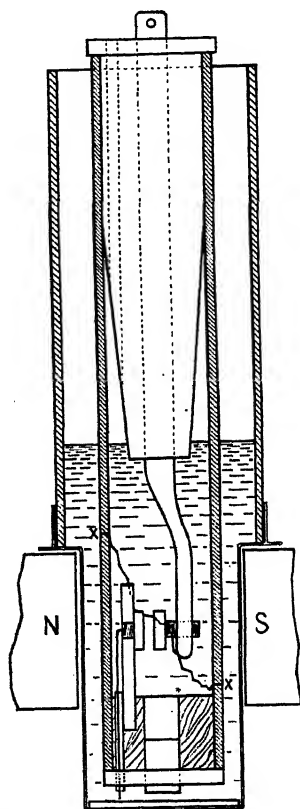


Fig. 5. Abandoned design of apparatus showing fracture x..x.

Consequently the author approached Prof. Smouloff and the following practical tests have up to date been carried out conjointly by Prof. Smouloff and the author in the laboratories of the Electrotechnical Institute in Leningrad, using the special apparatus of the author's design shown in Figs. 4, 5 and 6.

The fact seems worth recording that the first form in which this apparatus was designed was as shown in Fig. 4. This apparatus gave perfectly satisfactory results using voltages up to even 50,000 volts as long as no magnetic field was involved.

\* "The Physical Nature of Dielectric Breakdown," a paper read before the International High Tension Conference in Paris in 1927.

With a strong magnetic field excited with D.C. current the glass tube fractured at the position marked *xx* when the voltage reached 38,000–40,000 volts. New glasses and specially annealed glass tubes were cut and fitted three times but with the same result each time. The apparatus shown in Fig. 5 was developed with oil surrounding the glass tube in such a manner as to eliminate corona and mechanical pressure, but the same trouble due to the cracking of the glass tube as soon as the voltage reached a value of approximately 40,000 volts with a superimposed D.C. magnetic field was encountered. This set-back in making up the apparatus in itself appears to reveal a phenomenon worthy of further investigation and probably

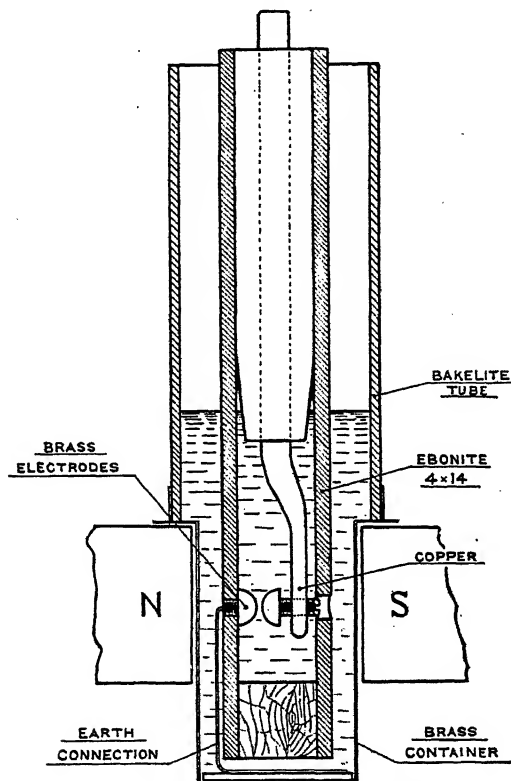


Fig. 6. Improved design of apparatus.

explainable by the theory of the behaviour of electrons in dielectric and magnetic fields which has been advanced by Prof. Smouloff.

The test gap was so made that it could be placed in the air gap of a specially adapted transformer yoke (which was utilised for producing suitable magnetic fields) and could be turned in the gap so that the magnetic field was either transverse or parallel to the dielectric field.

The materials available for preliminary tests were none of them what might be called good dielectrics, hence it was decided to make the preliminary tests described below on:

- (1) Air at ordinary laboratory temperature, pressure and humidity.
- (2) Transformer oil (commercially dry).
- (3) Pressboard (as representing a commercial dielectric and one of comparatively poor quality although extensively used).
- (4) Sulphur as representing a good dielectric the properties of which are well known.

#### TESTS ON AIR

The first results obtained when testing the breakdown strength of air were so extraordinarily contradictory that it was difficult to find any explanation for their divergencies. The results of some 293 tests are represented by the curves in Fig. 7 in which air gap has been plotted against percentage decrease and percentage

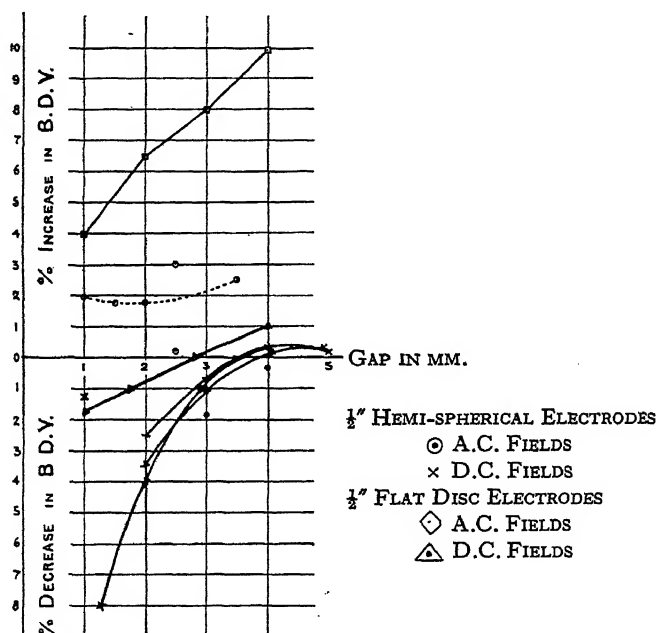


Fig. 7. Effect of transverse magnetic fields on breakdown voltage of air.  
Laboratory temperature 18°0 C.

increase in breakdown voltage under the influence of various magnetic fields. These curves all show that the length of the spark gap appreciably influences the effect of a superimposed magnetic field on the breakdown voltage of fluids.

This result is of much interest because it would appear that there are other influences at work which tend to mask the real decrease in breakdown strength under the influence of a magnetic field which it is reasonable to expect if the conclusion reached by Prof. Smouloff in a recent paper\* be accepted.

The character and the sound of the arc during discharge varied appreciably

\* "The Physical Nature of the Phenomena in Homogeneous Dielectrics," read before the International Mathematical Conference at Bologna in September 1928.

when tests were made with and without strong magnetic fields, hence the conclusion was reached that the masking of the decrease in breakdown strength due to the deflection of electrons in their normal orbits (anticipated by Prof. Smouloff) was due to electrodynamic forces deflecting the leakage currents which flow through the dielectrics prior to breakdown and so extending their paths as to increase the sparking voltage. This masking effect might be expected to increase with the length of the gap, as the curves in Fig. 7 show. It is moreover also evident from Fig. 7 that the influence of the spark gap length is greater with A.C. than with D.C. magnetic fields. This too might be expected, as the blow-out effect of an A.C. magnetic field in phase with the dielectric field will be greater than that of a corresponding D.C. field on the same A.C. dielectric field.

Tests were also made with the hemispherical electrodes arranged so that the dielectric field was parallel to the magnetic field. In this case the results (as seen from Table IV) showed a decrease in breakdown voltage for both A.C. and D.C. fields which in the latter case approximately corresponded to that observed with a transverse field.

Table IV: Tests on air.

Gap in mm.	Excitation of magnet	Excitation current in amps	No. of tests	% decrease in electric strength with magnetic field
1.80	A.C.	11	10	2.5
1.95	D.C.	16.4	10	2.5

## TESTS ON OIL

The majority of the tests on oil were made with commercially dry oil, i.e. not on oil which had been specially dried to give it an electric strength higher than that obtaining in ordinary electric high tension work.

It was found that on any particular sample of oil the first ten tests made gave results which varied over a wide range, but that after ten tests apparently the moisture in the neighbourhood of the gap had been attracted into the gap and dispersed by the discharges so that the sample improved in strength and finally gave the most extraordinarily uniform results, even although a further 60 or 70 tests might be made. Table V shows a typical example of such a test. In this case

Table V: Tests on oil.

Gap in mm.	Arrangement of gap	Magnetic field current (amps)	Average 5 tests without field	Average 5 tests with field	% increase with magnetic field	% decrease with magnetic field
2	Longitudinal	A.C. 21.5	18500	20800	8.9	—
2	"	"	22060	23140	9.5	—
2	"	"	23140	23850	9.7	—
2	"	"	20720	23400	8.9	—
2	"	"	20940	23080	9.1	—
2	Transverse	A.C. 21.5	20500	23060	8.9	—
2	"	D.C. 16	20400	17550	—	8.6
2	"	"	19180	17200	—	9.0
2	"	"	20450	18430	—	9.0
2	"	"	20400	17500	—	8.6



it will be seen that the A.C. field, whether transverse or longitudinal, had the effect of increasing the breakdown strength of the oil. This increase was however not observed in other tests made with a weaker A.C. field and with greater gap settings. The application of a D.C. field resulted in a decrease of the breakdown value of the oil under test.

The above results of tests on oil confirm the observations made in the tests on air: i.e. the electrodynamic forces acting on the leakage currents through the dielectric before breakdown occurs appear to increase their path and hence increase the sparking voltage so that the decrease in sparking voltage due to the effect described by Prof. Smouloff is masked.

#### TESTS ON PRESSBOARD

The tests on pressboard were made on specially prepared small samples cut from good quality pressboard and subjected to normal conditioning according to E.R.A. rules before the tests were made.

The results of these tests showed that with both D.C. and A.C. transverse fields there was comparatively little effect produced, but with a D.C. longitudinal field the decrease in the breakdown strength of the material was 27.5 per cent. and in the case of an A.C. field the average decrease in breakdown strength was 23.4 per cent., the figures being as in Table VI.

Table VI: Tests on pressboard.

Breakdown voltage without field	Breakdown voltage with A.C. field	Breakdown voltage with D.C. field
23700	18000	15500
23600	19000	16300
17400	16800	19400
18400	17700	16400
23900	14800	14600
23600	14000	14400
20000	18600	16000
23500	17200	
24000		
24000		
222100	136100	112600
Average 22210	17012	16085
Percentage decrease with magnetic field	23.4	27.5

In making this test it was observed that the comparatively small residual magnetism in the core of the test magnet was sufficient to affect the result, and hence the core had to be demagnetized with A.C. before reliable readings of breakdown strength without field could be obtained.

These tests on air, oil and pressboard were sufficiently convincing to indicate that the presence of a magnetic field had a very marked effect on the characteristics of dielectrics, but that the measurement of breakdown voltage as a means of indicating this effect was unsatisfactory because other effects entered into the test which could not be accurately determined. Consequently further tests using sulphur, etc. were

abandoned and plans were made for measurement of dielectric losses in various dielectrics under the influence of both A.C. and D.C. fields of varying intensity. These tests are proceeding and will form the subject of a subsequent paper. Preliminary tests have shown that under certain conditions the dielectric losses may be increased in a dielectric as much as 30–35 per cent. by the presence of a magnetic field. The mathematical treatment of the subject by Prof. Smouloff in his paper referred to above would indicate that effects of this magnitude are to be expected.

# A NEW ALTERNATING CURRENT POTENTIOMETER OF LARSEN TYPE

By ALBERT CAMPBELL, M.A.

*Received November 8, 1928. Read and discussed November 23, 1928.*

**ABSTRACT.** The instrument is a modification of the simple Larsen A.C. Potentiometer, in which the unknown voltage is balanced by another ( $v_2$ ) of the form  $(r + j\omega m) i_1$ , where  $i_1$  is a constant standard current and  $r$  and  $m$  are resistance and mutual inductance, both variable. In the simple type the quadrature component  $\omega m i_1$  is obtained by multiplying the observed  $m i_1$  by the pulsance  $\omega$  (i.e.  $2\pi \times$  frequency). The new system avoids this trouble by ensuring that at any given frequency the current through the primary of the mutual inductance shall be such a multiple of  $i_1$  as to make the balancing voltage  $(r + jbM) i_1$  where  $M$  is the mutual inductance and  $b$  a constant. This is achieved by an arrangement of loop-shunt, which can be set for any given frequency so that the readings of  $r$  and  $bM$  shall give the two components directly in millivolts. The standard alternating current  $i_1$  is set and held constant by a thermal null method in which it is balanced against a known direct current.

## § 1. HISTORICAL INTRODUCTION

MANY years ago the author showed\* how impure mutual inductances (and iron-cored current transformers) could be tested by balancing the secondary voltage by means of the simple combination of variable resistance  $r$  and mutual inductance  $m$  shown in Fig. 1.

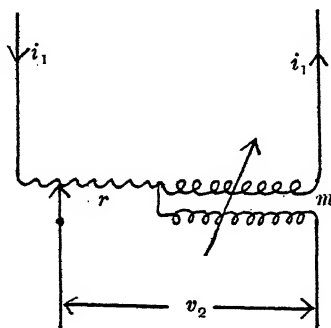


Fig. 1. Simple Larsen potentiometer.

Not long afterwards Sharp and Crawford† published methods of testing current transformers, which utilised a similar combination of  $r$  and  $m$ , and one of their elegant methods still remains the best for the purpose.

\* A. Campbell, *N.P.L. Report for 1908* (March 1909) and *Proc. Phys. Soc.* 22, 214 (1910).

† C. H. Sharp (In *Discussion*, June 30, 1909), *Am. I.E.E. Trans.* 28 (2), 1040 (1910) and later.

From the author's particular application of the  $(r, m)$  combination, Professor Larsen almost immediately recognised its much more general use and turned it into his beautifully simple A.C. potentiometer\*, in which an unknown voltage is balanced by  $v_2$  (Fig. 1) which is equal to  $(r + j\omega m) i_1$  where  $i_1$  is an alternating current held constant in magnitude and phase.

## § 2. THE NEW SHUNT SYSTEM

In the simple Larsen system the in-phase and quadrature components of the unknown voltage are given by  $ri_1$  and  $\omega mi_1$  respectively, and so, to obtain the latter, it is necessary to multiply the  $m$ -reading by the pulsance  $\omega$ , got by a knowledge of the frequency. The main object of the new system is to avoid this multiplication and thus make the instrument read the two component voltages directly.

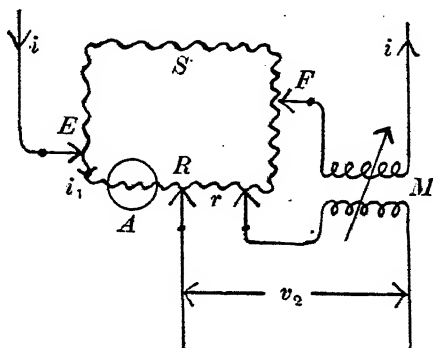


Fig. 2. Loop-shunt system.

The arrangement by which this simplification is attained† is shown in Fig. 2. The supply current (of instantaneous value  $i$ ) divides itself between the branches  $R$  and  $S$  of a loop-shunt with sliders keeping  $(R + S)$  constant; it then passes on through the primary (invariable) circuit of the mutual inductor, which by adjustment of its secondary circuit can give continuous variation of  $M$  from a small negative value up to a large positive one. The in-phase component is taken across  $r$ , which is of ordinary potentiometer type with appropriate sliders and change-over switches, forming part of the arm  $R$ , which also includes a current-measuring device  $A$ , to be described below. Let  $i_1$  be the current in the arm  $R$ , and  $v_2$  the resultant voltage for balancing the unknown one. Also let the constant  $(R + S) = 2a$ .

$$\text{Then} \quad v_2 = ri_1 + j\omega Mi \quad \dots\dots(1).$$

$$\text{Now} \quad i = i_1 (R + S)/S;$$

so that if the ratio of  $S$  to  $R$  is set so as to make  $S/(R + S)$  equal to  $\omega/b$ , we have

$$v_2 = (r + jbM) i_1 \quad \dots\dots(2),$$

\* A. Larsen, *Elekt. Zeits.* 12, 1039 (1910).

† British Patent Specification 294,053.

where  $b$  is constant for this setting. When the frequency is known, it is only necessary to set the loop-sliders  $E$  and  $F$  so that

$$S = 2a\omega/b \quad \dots\dots(3),$$

and  $S$  can be graduated to read directly in  $n$  or in  $\omega$ . It will be noticed that the loop-shunt system is ideal for this purpose, as it only requires the resistance  $S$  to be set directly proportional to the frequency. The constant  $b$  is chosen so as to make the inductor part read in the same units as the  $r$ -part.

### § 3. STANDARDISATION OF THE REFERENCE CURRENT

In order that the readings of  $r$  and  $M$  may give absolute values for  $v_2$ , the reference current  $i_1$  must be set and held at a constant known value. This is done by comparison with a standard direct current (set by resistance and standard cell), using the device marked  $A$  in Fig. 2. It works by an extension (to alternating current) of a null method which the author has already published\*, and is shown in Fig. 3. It consists of a heater  $H$ , a thermopile  $Th$  with d.c. galvanometer  $G$ ,

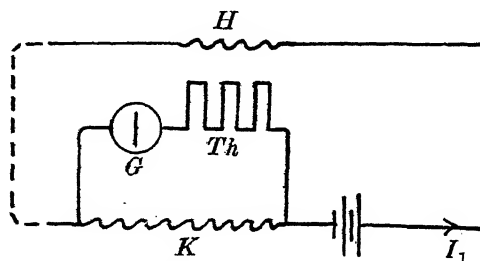


Fig. 3. Current-standardisation circuits.

and a low resistance  $K$ . In order to set and hold the alternating current  $i_1$  at a desired value  $I_1$ , direct current of the value  $I_1$  is first sent through  $H$  and  $K$ ,  $K$  being of such a value as to give zero reading on the galvanometer. (The voltage drop in  $K$  balances the thermal voltage in  $Th$ .) Then the direct current is switched off from  $H$  through an equal resistance so as still to maintain its value  $I_1$  through  $K$ , and the alternating current  $i_1$  is sent through  $H$  and adjusted until balance is again attained on the galvanometer. When this occurs,  $i_1$  will have the correct value  $I_1$  and, as long as the auxiliary direct current remains unchanged, can be held at this value by keeping the galvanometer deflection zero. An accuracy of 1 part in 1000 can be got if the alternating current source is steady enough. The standard reference current  $i_1$  is 10 milliamperes.

### § 4. CONSTRUCTION AND CAPABILITIES OF THE INSTRUMENT

The actual instrument, which is made by The Cambridge Instrument Co., is shown in Fig. 4. The  $r$ -part reading the in-phase component has a range up to 1.8 volts and can be read to about 0.00001 volt; it can also be used as a direct

\* *I.E.E. Journal*, 30, 889 (1901).

current potentiometer. The  $m$ -part, for the quadrature component, consists of one of the author's new type inductometers with scale of constant percentage accuracy. It has extremely small impurity and can be used as a separate instrument. It gives a range up to 1 volt, readable to about 10 microvolts; for very small values it can be read to about 2 microvolts. Thus, by the use of a resistance of 100 ohms, currents of a few microamperes can be measured.

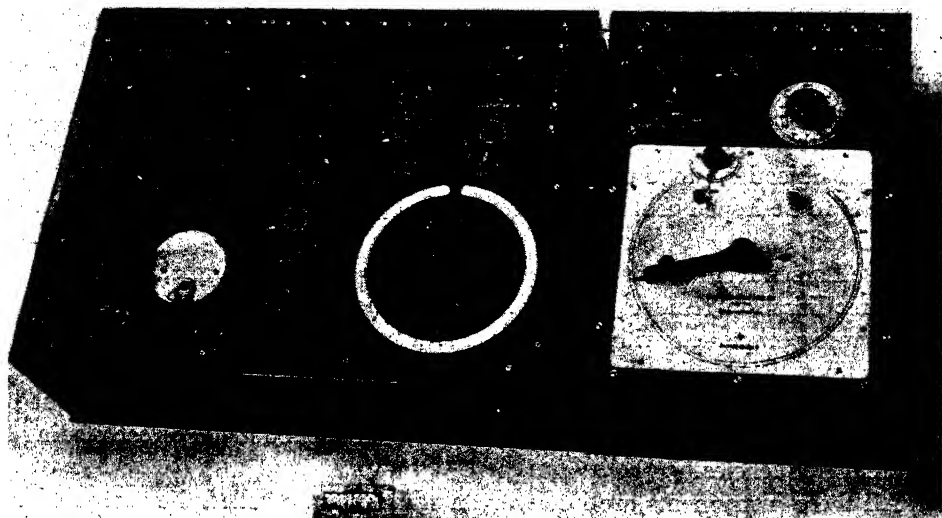


Fig. 4. Campbell-Larsen A.C. potentiometer.

The frequency-setting part can be set with an accuracy of at least 1 in 1000 at any part of its range from 25 up to 1000 cycles per sec. Higher frequencies require a simple multiplier to be used. Coarse and fine rheostats for the alternating current and direct current circuits are included in the instrument, and there is a switch which reverses one or both of the components of  $v_2$ , indicating automatically in which quadrant the phase-angle  $\tan^{-1}(M/r)$  lies. The detecting instrument is usually a telephone or vibration galvanometer.

The author's best thanks are due to Mr W. L. Beck for the skilful manner in which the details of construction have been planned and carried out.

NOTE ADDED NOVEMBER 25, 1928

Reference should be made to two other potentiometers in which the Larsen system is used with devices somewhat similar to the author's arrangement: W. Geyger, *Arch. f. Electrot.* 13, 80 (1924), and A. Pagès, *Société d'Études pour Liaisons Téléphoniques etc.*, Sept. 25, 1925.

## DISCUSSION

Dr DRYSDALE: I must congratulate Mr Campbell heartily on his great improvement on the Larsen potentiometer and I am glad to see that he has brought the subject of A.C. potentiometers again before the Society, as their value has never been sufficiently appreciated in this country. A.C. measurements are now the most important part of electrical testing and involve a very large amount of costly apparatus, so that a single instrument which enables nearly the whole range of such tests to be made within an accuracy of one or two tenths per cent., using only a simple volt box and set of non-inductive "shunts" seems to be most desirable. This has been appreciated in many countries, more especially in Japan, but there still seems to be an impression in this country that A.C. potentiometers are complicated and difficult to use, and of doubtful accuracy. Modern A.C. supplies however are so good both for wave-form and constancy of frequency that the principal objections to the use of A.C. potentiometers have largely disappeared, and it is to be hoped that their extreme adaptability will become more generally appreciated.

The Larsen form of potentiometer is certainly the most simple, and Mr Campbell's modification removes the principal objection to it (that of variation of the quadrature component with frequency), and makes it direct reading. Mr Gall's "co-ordinate" potentiometer secures the same result by preliminary adjustment of the phase-splitting device; but the Pedersen potentiometer, in which the quadrature relation is independent of frequency, cannot easily be made direct reading for different frequencies.

All these instruments are however on what may be called the rectangular or Cartesian principle in which the components  $x$  and  $y$  of the vector voltage are measured and its magnitude is obtained as  $\sqrt{x^2 + y^2}$  while the phase angle  $\theta$  is obtained as  $\tan^{-1} y/x$ . In actual testing it is much more convenient to measure the magnitude and phase of the voltage directly, and the Drysdale-Tinsley potentiometer which effects this would still seem to be the most useful all-round instrument, although there are a few cases, such as the measurement of very small phase angles nearly in phase or in quadrature with the supply, where the rectangular principle is more accurate. But the comparison of the two methods can best be visualised by realising that A.C. measurements are analogous to surveying, and that the rectangular co-ordinate principle is equivalent to being able only to make measurements, say of a house, along N.S. or E.W. directions, instead of being able to measure off the length along the walls directly and finding their directions (if necessary) by a theodolite. The phase-shifting transformer of the polar potentiometer corresponds to the theodolite; and as it is provided with cross pointers which enable the cosine and sine of the phase angle, as well as the angle itself, to be read off directly, it makes the calculation of the rectangular components or the equivalent resistance and reactance very easy.

I especially admire Mr Campbell's beautiful and effective thermal method of securing constancy of current as it is quite non-inductive and absorbs much less

power than the dynamometer which has been employed in my own potentiometer. On the other hand, the dynamometer does not require an auxiliary constant direct current.

I hope that Mr Campbell's interesting paper will prove a stimulus towards the employment of A.C. potentiometers in all testing laboratories.

Dr A. H. DAVIS: Such a potentiometer should be very suitable for the type of acoustical work in which the distribution, transmission, reflection, etc. of sound is measured by means of electrical microphones, the source of sound being a loud-speaker actuated by A.C. of pure wave-form. Mr Campbell's potentiometer measures E.M.F.'s of the magnitude and frequency ranges ordinarily met with in work of the kind, and the supply current  $i$  for the potentiometer can be obtained direct from the loud-speaker circuit. The potentiometer null method of measurement is especially advantageous where irregular extraneous disturbances are picked up by the leads from neighbouring X-ray outfits, power mains, etc. Being transients they cannot be satisfactorily eliminated by tuning devices, but with a telephone as detector it is possible to listen to the disappearance of the test note even in the presence of interference which would otherwise be prohibitive. Mr Campbell's loop shunt neatly facilitates the calculation of the phase and resultant from the readings of the instrument, and the operation can be performed readily—without summing squares—on an ordinary slide rule having trigonometric functions on the slider. For  $\theta$  is found as  $\tan^{-1} Y/X$  and then  $R$  is found as  $Y/\sin \theta$ .

The PRESIDENT: The subject of A.C. measurement has been so important for many years that a vast amount of study has been given to it, and one would think that nothing more could be done by the mere devising of circuits; but Mr Campbell has shown that the subject is not exhausted, that improvements can still be imported into apparatus and methods, and, what is noteworthy, his new improvement makes for simplicity and not for complexity.

AUTHOR's reply: Dr Drysdale has very clearly indicated the differences between the two types of A.C. potentiometer. Each type has advantages for particular kinds of test work. The Larsen type is of special advantage at the higher audio-frequencies, as it requires no phase-splitting device and uses a very small amount of power for its operation. I agree with Dr Davis that it is ideal for many acoustical investigations. I would emphasise the importance of the instrument for the accurate measurement of very small voltages and current (e.g. a few micro-amperes). In both cases the scale does not follow the square law, but gives direct proportionality, which is an enormous gain at the low readings.



# FERROMAGNETIC FERRIC OXIDE

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**ABSTRACT.** A brief account is given of work relating to the above subject that has been published during the past eight years. The authors confirm the observation by Messrs. Sosman and Posnjak that lepidocrocite, but not gothite, yields on dehydration a strongly ferromagnetic ferric oxide. As all the specimens of lepidocrocite examined contained three or four per cent. of manganese oxide, they suggest that this substance may be an essential constituent of this crystalline form of the hydrate. They find that the temperature at which the ferromagnetic oxide is permanently transformed into the common paramagnetic kind is largely dependent upon its mode of preparation.

A table showing the magnetic force at which the magnetic permeability and susceptibility reach their maximum values as well as the coercive force and remanent magnetisation is given for different kinds of magnetic ferric oxide and for magnesium and copper ferrites in the form of compressed rectangular bars. Comparative figures are given for two varieties of natural magnetite. Curves are also given showing the variation of permeability with field strengths ranging from 25 to 1300 C.G.S. units.

Although copper ferrite has a higher maximum permeability than ordinary precipitated magnetic oxide of iron, it falls far below that of the purer forms of native magnetite. Analyses of several natural magnetites are given, and the high or low values of the susceptibility of the ferric oxide resulting from their oxidation are attributed to the presence or absence of impurities, particularly magnesia which forms a magnetic ferrite.

## § 1. INTRODUCTION

IN a paper read to this Society in 1921 on "The Magnetic Susceptibility of Certain Natural and Artificial Oxides\*," we drew attention to the very great range of magnetic susceptibility exhibited by ferric oxide in its different forms, and gave references to the discovery of a magnetic form of ferric oxide by Robbins in 1859†, and to the subsequent observations of Malaguti‡ and Liversidge§.

During the past few years further work on this subject has been published; in 1925 L. A. Welo and O. Baudisch||, using a ballistic galvanometer method in which the oxides in the form of powder were packed "by jarring" in a glass tube 20 cms. long, compared the permeability of precipitated magnetic oxide,  $\text{Fe}_3\text{O}_4$ , with magnetic  $\text{Fe}_2\text{O}_3$  derived from it by heating the former to 220° C. in air. They found

\* *Proc. Phys. Soc.* 33, 196-205 (1921).

† *Chemical News*, 1, 11, 1859.

‡ *Ann. de Chim. et de Phys.* ser. 3, 69, 214.

§ *Trans. Aust. Assoc. Hobart Meeting*, 1892.

|| *Phil. Mag.* 50, 399-408 (1925).

an increase in the maximum permeability from 2.93 to 3.39 after this conversion and noted that heating in nitrogen to 550° C. caused a reduction in permeability to near the value for ordinary normal haematite, while magnetite could be heated in an inert atmosphere to 800° C. without loss of permeability after it regained normal temperature. They conclude that the extra oxygen required to convert  $2\text{Fe}_3\text{O}_4$  into  $3\text{Fe}_2\text{O}_3$  can be introduced without undue strain, leaving the structure essentially unaltered. Figures derived from X-ray analysis are given in support of this view of the identity of crystal structure of  $\text{Fe}_3\text{O}_4$  and ferromagnetic  $\text{Fe}_2\text{O}_3$ .

Later in the same year (1925) R. B. Sosman and E. Posnjak\* published, under the same title as this communication, the results of their investigation of a naturally occurring ferromagnetic ferric oxide, found in Shasta County, California, which they received from Graton and Butler. The fact that they regarded this discovery of a natural form of magnetic ferric oxide as very unusual and noteworthy increases our reluctance to accept the statement of S. Hilpert† that “one finds in nature large deposits of strongly magnetic  $\text{Fe}_2\text{O}_3$  derived from the oxidation of ferrous compounds.” It is a matter for regret that Hilpert did not specify any locality where this native magnetic ferric oxide was known to occur. Our own experience and examination of iron ores extending over many years inclines us to the belief that Sosman and Posnjak’s view that it is very exceptional is the more correct one. These authors have also found that on dehydrating by moderate heating the two crystalline forms of native monohydrated ferric oxide, gothite and lepidocrocite, the former yielded only the paramagnetic form, while the latter gave a strongly ferromagnetic ferric oxide. This difference in behaviour they suggest is due to difference in the initial crystalline form. Without necessarily accepting this or any other theoretical explanation we can confirm the fact of the marked difference in behaviour of these two crystalline hydrates. These authors have also compared the magnetic susceptibility of both the native ferric oxide and that produced artificially by oxidising precipitated magnetic oxide, with finely powdered natural magnetite from Mineville, N.Y. They do not appear to have found any marked difference in susceptibility between natural and artificial magnetite, nor between them and the magnetic form of ferric oxide, but they show that these have different hysteresis loops and thus indicate that the remanence and coercive force of magnetic ferric oxide are higher than those of Mineville magnetite. But it must be clearly realised that had they used some other form of natural magnetite, such as some specimens from Arkansas‡, the results of this comparison would have been quite different—in fact, the reverse of what they say. They emphasise the difficulties of comparing the susceptibilities of powders so soon as a moderately high value has been reached, and we have ourselves suggested the figure for the mass susceptibility of 0.01 C.G.S. unit as about the limit for which any method employing the pull of a non-homogeneous field can be trusted. The factors which they mention, viz. “fineness of grain, shape of grains, size and shape of the charge as a whole and previous magnetic

\* *Journ. Wash. Acad.* 15, no. 14 (Aug. 1925).

† *Deut. Chem. Ges. Ber.* 42, B 2, 2248–61 (1909).

‡ *Proc. Phys. Soc.* 31, 311 (1919).

history" are all of importance as there is an "end-effect" of the mass as a whole apart from that of its constituent grains and the distortion of the field consequent upon the introduction of any appreciable mass of highly permeable material. These considerations have led us to abandon the modified Curie balance when comparing the higher susceptibilities dealt with later.

While we are in general agreement with Sosman and Posnjak's paper, there are two statements in it that appear to require qualification. One is that ferromagnetic ferric oxide is completely changed into the paramagnetic form by heating *for a few minutes* to  $650^{\circ}\text{C}.$ ; the other that the ferromagnetic form has a distinctive colour "further toward the yellow than the paramagnetic and of a slightly darker shade, and so tends toward a chocolate brown color." Both of these statements may be, and probably are, true when applied to the ferric oxide obtained by oxidising precipitated magnetic oxide in suspension by ammonium persulphate solution, or by prolonged exposure to air in a moist state with or without moderate heating. But examples will be mentioned and exhibited showing that the colour may vary from a full red to the colder yellowish brown and also that some forms of magnetic  $\text{Fe}_2\text{O}_3$  require a higher temperature than  $650^{\circ}\text{C}.$ , or a much more prolonged heating to convert them into the paramagnetic form.

In a paper in the *Comptes Rendus*\*, R. Chevallier describes his method of preparing ferromagnetic ferric oxide and to some extent his method of measuring or comparing the susceptibilities. He states that the field strength employed was 174 gauss and that he used a ballistic galvanometer method and measured the throw on making or breaking the primary current, but nowhere in the paper is any mention made of the inductive throw produced when no specimen is present (air core reading), nor are his galvanometer deflections given as differences or excesses over the air core throw. We therefore find it extremely difficult to interpret the results of his measurements. He concludes that magnetic oxide and ferromagnetic ferric oxide have substantially the same susceptibility, but that the latter has a greater permanent magnetisation in the ratio of 6.15 : 3.8. He states that this ferric oxide loses its magnetic properties rapidly between  $600^{\circ}$  and  $700^{\circ}\text{C}.$ , but that it never loses them entirely. In fact, if one heats it for a quarter of an hour to near  $900^{\circ}\text{C}.$  one obtains afresh a black, very ferromagnetic powder. This he attributes to the reconversion of  $\text{Fe}_2\text{O}_3$  into  $\text{Fe}_3\text{O}_4$  (*La décomposition de  $\text{Fe}_2\text{O}_3$  en magnétite doit alors intervenir et limiter la disparition du magnétisme*). This supposed conversion of ferric oxide into magnetic oxide by merely heating *in air* to  $900^{\circ}\text{C}.$  is entirely opposed to all chemical knowledge of the stability of  $\text{Fe}_2\text{O}_3$  in regard to oxygen, but may have been caused by the accidental introduction of reducing gases which the use of an electric furnace would have avoided. It is of course well known that heating most forms of ferric oxide for an appreciable time to  $900^{\circ}$  or  $1000^{\circ}\text{C}.$  will permanently change their colour to black or nearly black, but this physical change is not associated with any chemical alteration of the  $\text{Fe}_2\text{O}_3$  nor in the case of pure oxide with any appreciable increase in susceptibility. The lowest susceptibility for substantially pure ferric oxide we have yet found was  $15.2 \times 10^{-6}$  in

\* *Comp. Rend.* T. 180, 1473-5 (1925).

the case of a good specimen of colcothar, or rouge, after heating to 1000° C. for half an hour, and its colour was then quite black. The method of preparation of this magnetic form of  $\text{Fe}_2\text{O}_3$  employed by Chevallier consisted in heating the magnetic oxide—evidently the precipitated form—to about 350° C. when the oxide takes fire in air and this spreads rapidly throughout the mass.

In contrast with this method, H. Abraham and Planiol in a slightly earlier paper in the *Comptes Rendus*\*, describe the preparation of ferromagnetic  $\text{Fe}_2\text{O}_3$  by the reduction of  $\text{Fe}_2\text{O}_3$  to  $\text{Fe}_3\text{O}_4$  in hydrogen or carbon monoxide at 500° C. This  $\text{Fe}_3\text{O}_4$  is not pyrophoric but is very easily oxidised and can give either the red ferric oxide ("colcotar") or magnetic ferric oxide; if burnt in air it burns like tinder and gives only the former, but if it be oxidised slowly in a current of air at 200°–250° C. there is no incandescence and the product is a brown powder somewhat yellowish, strongly ferromagnetic, and nearly like magnetite in its magnetic properties. Alteration to non-magnetic  $\text{Fe}_2\text{O}_3$  does not appear at 600° C. but appears slowly at 650°, and towards 700° the transformation is complete.

In a paper on "The Thermomagnetic study of certain Iron Minerals" by J. Huggett and G. Chaudron†, curves are given showing the variation of susceptibility with temperatures up to 700° C., but the magnitude of the applied magnetic force is not stated. The curve for magnetite shows a rapid fall near 570° C. (this is higher than that generally accepted as the temperature at which magnetite loses its ferromagnetic properties). They state in the paper that göthite heated without previous dehydration shows an increase near 350° C. *at the moment when the water leaves it*, and in this respect it resembles lepidocrocite; but the curve given for lepidocrocite is totally different from any other, showing that a little before 350° and up to just above 570° C. it acquires a very high susceptibility indeed and cannot be plotted on their scale. The statement that göthite after dehydration by heating to 600° C. in a vacuum exhibits a change in the curve at 570° C. thus showing that it contains 0.001 of magnetite is open to criticism. Unless supported by chemical examination this appears to us a mere assumption, and, even if ferrous iron were found after heating in a vacuum to 600° C., it does not follow that it was present in the original mineral, as it might have been formed by the reducing action of traces of organic matter that would be much more effective in a vacuum than on heating in air. No specimen of crystalline göthite examined by us contained any chemically detectable ferrous iron, and the measured susceptibility is so low as to exclude the possibility of 0.1 per cent. of magnetite in the natural mineral.

## § 2. OXIDATION OF MAGNETITE

Precipitated magnetic oxide of iron can be oxidised to  $\text{Fe}_2\text{O}_3$  while suspended in an alkaline solution by sodium hypochlorite or by ammonium persulphate, or by prolonged exposure in thin layers to the air in a moist state, or by moderate heating in a current of air. If previously dehydrated by heating in  $\text{CO}_2$  or nitrogen to a temperature of 400° to 500° C. after cooling it is more stable, but oxidation can

\* *Comp. Rend.* T. 180, 1328–9 (1925).

† *Ibid.* 186, 694–6 (1928).

still be brought about by heating in air to about  $350^{\circ}$  to  $400^{\circ}$  C. Native magnetite is much more resistant to oxidation, even when reduced to very fine powder in an agate mortar, and different varieties exhibit great differences in their resistance to oxidation\*. Some forms require to be heated for some hours to a temperature of  $1000^{\circ}$  C. in order to oxidise them completely.

The difference in the magnetic susceptibility of the resulting ferric oxide, even when the latter was shown by chemical examination to be free from ferrous iron, presented a very puzzling problem. A purchased specimen of precipitated  $\text{Fe}_3\text{O}_4$  was found on oxidation to give a highly magnetic ferric oxide as anticipated, but this  $\text{Fe}_2\text{O}_3$  after heating for an hour at  $1060^{\circ}$  C. in the open quartz tube of an electric furnace still gave a  $k_m$ † value of  $3500 \times 10^{-6}$ , and was "evidently magnetic," i.e., its particles would cling readily to the pole of a small bar magnet. Chemical examination of the  $\text{Fe}_3\text{O}_4$  from which it was derived showed small but very evident traces of calcium carbonate, indicating that the iron salts from which it was derived had been precipitated by slaked lime. After removal of the calcium carbonate by treatment with dilute acetic or very dilute nitric acid, washing and drying this purified  $\text{Fe}_3\text{O}_4$ , it still yielded an equally magnetic ferric oxide when oxidised in air at about  $400^{\circ}$  C., but its  $k_m$  value now fell to  $196 \times 10^{-6}$  after heating for two hours at  $750^{\circ}$  C., and after a similar time at  $1050^{\circ}$  it had fallen to  $44.3 \times 10^{-6}$ . It thus appeared that calcium carbonate, by forming calcium ferrite, might prevent the loss of magnetic properties of ferromagnetic  $\text{Fe}_2\text{O}_3$  on prolonged heating. Forestier and Chaudron‡ have stated that calcium ferrite is rendered irreversibly non-magnetic by heating to above  $700^{\circ}$  C. This statement led us to a re-examination of calcium ferrite: some calcium ferrite which had a  $k_m$  value of  $12,230 \times 10^{-6}$  units was heated for thirty minutes at  $900^{\circ}$  C., allowed to cool and its  $k_m$  value again found; it was now  $4650 \times 10^{-6}$  and was "evidently magnetic." It was then subjected for ten hours to a temperature ranging from  $1000^{\circ}$  to  $1050^{\circ}$  C., and after cooling its  $k_m$  value had fallen to  $1120 \times 10^{-6}$ . It is thus seen that the loss of magnetic properties of calcium ferrite is slow and incomplete, even at  $1000^{\circ}$  C. Small quantities of calcium salts may therefore give rise to enhanced susceptibility which is difficult to destroy by heating for considerable periods.

### § 3. NATURAL MAGNETITES

A piece of crystal from Traversella, Piedmont, was reduced to very fine powder in an agate mortar and heated in the electric furnace for four hours at  $1000^{\circ}$ – $1050^{\circ}$  C., after which it was examined chemically and showed no ferrous iron; yet its  $k_m$  value was over  $4000 \times 10^{-6}$  and it was "evidently magnetic." It was again heated to about  $1050^{\circ}$  C. for ten hours and after cooling it gave  $5410 \times 10^{-6}$  for its  $k_m$  value. The rate of cooling appeared to be influencing the result, and it was found that after heating to  $1040^{\circ}$  C. for a few minutes and quickly cooling, it gave  $6060 \times 10^{-6}$ , but if cooled very slowly its  $k_m$  was  $4546 \times 10^{-6}$ ; evidently it was still magnetic, yet completely oxidised.

\* Moissan, *Ann. de Chimie* (5), 21, 233.

† Throughout this paper  $k_m$  denotes the mass-susceptibility per gram.

‡ *Comp. Rend. T.* 181, 509–11 (1925).

*Magnetite from Mineville, New York State, U.S.A.* Through the kindness of Mr A. M. Cummings, the General Superintendent of Messrs Witherbee, Sherman and Co., we were supplied with some specimens of this magnetite. When finely powdered it oxidised easily in air at  $1030^{\circ}$ – $1060^{\circ}$  C. and after three hours' heating at this temperature it was found to contain no detectable ferrous iron. Its  $k_m$  value was reduced to  $52 \times 10^{-6}$ , and a further heating at the above temperature merely reduced this already low figure to  $47 \times 10^{-6}$ . This result was in marked contrast with the oxidation product of Traversella magnetite.

*Altenfjord (Norway) magnetite* similarly treated oxidised fairly easily and gave a product with a  $k_m$  value of  $71.5 \times 10^{-6}$ . It contained inclusions of feldspar.

*Two varieties of magnetite from the Tilly Foster mine, New York*, are described elsewhere as Tilly Foster I and II. No. I gave after oxidising at  $1000^{\circ}$  C. a product with a  $k_m$  value of  $71 \times 10^{-6}$ . (This product was dark purplish slate, not quite black.) No. II after four hours' heating at  $1000^{\circ}$ – $1066^{\circ}$  C. gave a product chemically free from ferrous iron, but with a  $k_m$  value of  $8700 \times 10^{-6}$ . Repowdering and reheating scarcely altered this value, which then became  $8110 \times 10^{-6}$ .

*Penryn (Cornwall) magnetite*, after heating for four hours as in previous cases, was found to be fully oxidised and its  $k_m$  value was  $220 \times 10^{-6}$ .

*Arkansas magnetite*, after treatment as in other cases, gave an oxidised product with a  $k_m$  value of  $2760 \times 10^{-6}$ .

The problem thus presented is why some magnetites like that from Mineville on being fully oxidised gave a ferric oxide of quite low susceptibility ( $47 \times 10^{-6}$ ), while others such as Traversella and Tilly Foster II gave  $k_m$  values of 5000 to 6000 and  $8700 \times 10^{-6}$  respectively. The investigation of this problem involved the complete quantitative analysis of the above named magnetites. All details of analysis are omitted for lack of space, but the general (in some cases, average) results are given in Table I. The small and variable amounts of manganese found in all the specimens did not appear to have any relation to the magnetic properties of the final oxidation product, but a connexion was at once seen when the magnesium content was considered. In Mineville and Tilly Foster I it was absent, while in Tilly Foster II, Traversella and Arkansas it reached the values of 3.0, 1.9 and 4.5 per cent., respectively. That the percentage of MgO in the Arkansas specimens is not in proportion to the retained magnetic properties of the  $\text{Fe}_2\text{O}_3$  is probably due to the considerable amounts of titanitic acid and combined silicates, so that less of the MgO is available for the formation of a ferrite. Probably the presence of the  $\text{TiO}_2$  and other impurities may be connected with the very high coercive force (150) and relatively low permeability of this magnetite\*. It will be noticed that the ratio ( $\text{FeO} : \text{Fe}_2\text{O}_3$ ) is higher than that required for pure  $\text{Fe}_3\text{O}_4$  in this magnetite, thus indicating that a part of the FeO is combined with titanitic acid.

In Mineville magnetite the ratio  $\text{FeO} : \text{Fe}_2\text{O}_3$  is correct, showing that apart from unavoidable inclusions of quartz, it is practically pure  $\text{Fe}_3\text{O}_4$ . In the Traversella specimens this ratio is slightly too low, indicating a partial oxidation of this magnetite. The latter condition is very noticeable in Tilly Foster II, where the

\* *Phys. Soc. Proc., loc. cit.* (1919).

FeO : Fe<sub>2</sub>O<sub>3</sub> ratio falls to 0.368 instead of 0.45, while in Tilly Foster I the ratio is 0.44 or nearly normal. Penryn magnetite is also a partially oxidised one, giving the ratio of 0.375.

Table I: Chemical analysis of natural magnetites

Locality	Arkansas	Mineville, N.Y.	Traversella	Penryn (Cornwall)	Tilly Foster II (N.Y.)
FeO	26.48	30.7	28.4	25.1	25.8
Fe <sub>2</sub> O <sub>3</sub>	52.00	68.3	66.1	66.9	70.2
SiO <sub>2</sub>	2.25*	0.5†	2.34*	7.1*	Traces
TiO <sub>2</sub>	9.10	—	—	—	—
MgO	4.5	—	1.9	—	3.0†
MnO	1.49	0.05	0.103	0.015	0.09
Al <sub>2</sub> O <sub>3</sub>	4.1	—	—	—	—
	99.92	99.55	98.843	99.115	99.09

\* Including insoluble silicates.

† As quartz.

‡ Tilly Foster II contained traces of CaO in addition to MgO, and some CO<sub>2</sub> in combination with these bases.

Table I gives the approximate composition of some of the magnetites examined; in each case portions for analysis were obtained as free from visible inclusions as possible. The manganese was in most cases determined by a colorimetric method.

#### § 4. GÖTHITE AND LEPIDOCROCITE

These two minerals, which are supposed to have identical composition, namely Fe<sub>2</sub>O<sub>3</sub> · H<sub>2</sub>O, but different crystalline forms have been shown by Sosman and Posnjak, as above stated, to behave quite differently when dehydrated by moderate heating. Powdered göthite from Cornwall was found to give a  $k_m$  value of  $28.5 \times 10^{-6}$  in its original state. After heating to nearly 500° C. for fifteen minutes, its  $k_m$  value was raised to only  $33.2 \times 10^{-6}$ , and after half an hour at 750° C., this value fell to 21.1. Two and a half hours' heating at 1050° C. raised it again to the identical figure which it gave originally, namely 32.2; it was darker in colour, but still dark brown and not black.

Another specimen gave an initial  $k_m$  value of  $30.3 \times 10^{-6}$ ; after thirty minutes at 345° C. its  $k_m$  value reached  $39.8 \times 10^{-6}$ ; half an hour at 400° C. reduced it to  $34.7 \times 10^{-6}$ , and half an hour at 1000° reduced it still further to  $23.8 \times 10^{-6}$ . Thus both these typical specimens behaved similarly, and not unlike non-crystalline brown haematite which had an initial susceptibility of  $31.6 \times 10^{-6}$ , falling to  $27.3 \times 10^{-6}$  after thirty minutes at 375° C., and falling again to  $17.5 \times 10^{-6}$  after fifteen minutes at 750° C., and finally rising slightly to  $38 \times 10^{-6}$  after heating for thirty minutes at 1050° C. Its colour was then a dark reddish brown and, like göthite, it did not become black.

*Lepidocrocite.* The first specimen we examined was from Siegen, Westphalia. Its  $k_m$  value in the form of powder before heating was  $42 \times 10^{-6}$ ; after half an hour at 375° C. it gave a figure of  $39,500 \times 10^{-6}$ , i.e. so high that the modified Curie balance, which is excellent for low susceptibilities, became unsuitable and unreliable. After thirty minutes at 750° C. the susceptibility had fallen to  $129 \times 10^{-6}$ ,

but thirty minutes at  $1000^{\circ}\text{C}$ . raised it to  $392 \times 10^{-6}$ : its colour was now a very dark purplish brown, nearly black.

After some delay and difficulty, two other specimens of lepidocrocite from other localities were obtained; one came from Easton, Pennsylvania (the same locality from which the mineral used by Sosman and Posnjak was obtained), the other from Reading, Penn., U.S.A. Their magnetic changes were entirely similar to those of Siegen lepidocrocite, but the  $k_m$  value for the Reading specimen was rather lower.

Chemical examination of the specimens of göthite and lepidocrocite disclosed the fact that while in the case of the former there exists only a trace of manganese oxide (0.06 per cent.), in all three specimens of lepidocrocite from these widely different localities there is a considerable percentage of manganese in the form of a higher oxide (i.e. either  $\text{Mn}_2\text{O}_3$  or  $\text{MnO}_2$ ). In the Siegen specimen it was found to amount to 3.6 per cent., estimated gravimetrically as  $\text{Mn}_3\text{O}_4$ . In both the Easton and Reading specimens manganese is present to roughly a similar extent.

The presence of this amount of manganese accounts satisfactorily for two differences which lepidocrocite exhibits when compared with göthite. (1) The darker colour which its powder acquires after heating. (2) The higher final value for  $k_m$  after heating to above  $1000^{\circ}\text{C}$ ., namely  $392 \times 10^{-6}$  as compared with  $32.2$  or  $23.8 \times 10^{-6}$ . Can it account for the high  $k_m$  value reached on heating to  $350^{\circ}$ – $450^{\circ}\text{C}$ .? It does not seem possible that it can do so, not only on account of the very high value that is reached, but also because a mixture of the precipitated hydrated oxides when dehydrated at  $400^{\circ}\text{C}$ . does not give any appreciable rise in  $k_m$ , but does so on heating to  $750^{\circ}\text{C}$ ., and still more at  $1000^{\circ}\text{C}$ . Thus  $\text{MnO} \cdot \text{Fe}_2\text{O}_3$  is not formed at  $400^{\circ}$ , and when formed, the high  $k_m$  value persists even when the specimen is heated for four hours to temperatures above  $1000^{\circ}\text{C}$ . This is entirely at variance with the general behaviour of lepidocrocite, excepting only the retention of a small increase in the final value after  $1000^{\circ}\text{C}$ . over that of pure  $\text{Fe}_2\text{O}_3$ , due, no doubt, to the three to four per cent. of manganese oxide it contains. The suggestion of Sosman and Posnjak that the difference is primarily due to the difference in crystalline form would therefore appear the most probable explanation, were it not for the fact that while precipitated  $\text{Fe}_3\text{O}_4$  when fully hydrated is oxidised in aqueous suspension, it is practically as magnetic in that hydrated condition as when dehydrated.

Why, then, is not lepidocrocite magnetic as it occurs in nature, and why should it be necessary to dehydrate it? It may be that in its natural state it is not identical in crystal structure with magnetite, but can pass into that form on moderate heating, and it would be an interesting point for mineralogists to determine if three or four per cent. of manganese is essential to the formation of that crystalline variety that is called "lepidocrocite," or if the latter is ever known to occur in pure monohydrated ferric oxide.

Lepidocrocite that has been rendered ferromagnetic by heating for a few minutes at  $350^{\circ}$  to  $400^{\circ}\text{C}$ . is rapidly converted into the paramagnetic form when the temperature is raised. Heating for 35 minutes to  $480^{\circ}\text{C}$ . gave a reduced  $k_m$  value of only  $3000 \times 10^{-6}$ , or less than a tenth of its maximum. It is more easily converted



into the non-magnetic type than artificially produced  $\text{Fe}_2\text{O}_3$  from  $\text{Fe}_3\text{O}_4$  by low temperature oxidation, and the latter is less stable than that produced by the oxidation of ferrous oxide obtained by the calcination of ferrous oxalate in a closed crucible with subsequent admission of air, a little at a time. This last is highly magnetic, has usually a fine deep red colour, and is so resistant to heat that in an experiment in which both this oxide and Easton lepidocrocite were treated simultaneously in the same electric furnace, after ten minutes at  $650^\circ\text{C}$ . the  $k_m$  values were reduced from  $22,800 \times 10^{-6}$  to  $1900 \times 10^{-6}$  in the case of lepidocrocite, and from  $34,700 \times 10^{-6}$  to  $33,500 \times 10^{-6}$  with the  $\text{Fe}_2\text{O}_3$  from ferrous oxalate. Further heating for ten minutes at  $750^\circ\text{C}$ . caused the former to fall to  $68 \times 10^{-6}$  and the latter to  $7200 \times 10^{-6}$ ; the latter was now over a hundred times more magnetic than the former. There are thus great differences in the ease with which different forms of ferromagnetic ferric oxide pass into the common non-magnetic form.

*Artificial Hydrated Ferric Oxide.* Pure precipitated  $\text{Fe}_2\text{O}_3$  when dried at temperatures below  $100^\circ\text{C}$ . may have the composition of  $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$  or, like brown haematite, may be more nearly represented by the formula  $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ . The susceptibilities of these hydrates are always higher than that of the  $\text{Fe}_2\text{O}_3$  resulting from their dehydration (the exact opposite of the effect in lepidocrocite). The following values have been observed during this investigation: for  $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ , values ranging from  $127 \times 10^{-6}$  to  $147 \times 10^{-6}$ , and for approximately  $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ,  $102 \times 10^{-6}$  to  $115 \times 10^{-6}$  have been measured; while for anhydrous  $\text{Fe}_2\text{O}_3$ , the variation has been from  $21.1 \times 10^{-6}$  to  $33.8 \times 10^{-6}$ . As these may be regarded as equally pure, the only cause of variation is the mode of preparation having some obscure influence. It seems probable that precipitation at a high temperature with subsequent boiling gives rise to rather higher susceptibility than precipitation at a lower temperature and washing with cold water, but the observations are not conclusive. The minimum value for  $\text{Fe}_2\text{O}_3$  recorded above is  $21.1 \times 10^{-6}$ , and is slightly higher than that obtained from brown haematite after heating to  $750^\circ\text{C}$ . of  $17.5 \times 10^{-6}$ , and as already mentioned, the figure  $15.2 \times 10^{-6}$  for a black form resulting from heating a very good sample of rouge to  $1000^\circ\text{C}$ . is the lowest we have ever recorded for  $\text{Fe}_2\text{O}_3$  in any form. It is curious that the susceptibility of normal  $\text{Fe}_2\text{O}_3$  should be less than that of any of the oxides of Mn, Co or Ni.

Purchased hydrated ferric oxide is unfortunately in our experience unsuitable for magnetic work; besides containing frequently an appreciable quantity of calcium carbonate, it sometimes contains a trace of some organic substance (possibly derived from methylated spirit) which when the oxide is heated in a confined space, or in a large bulk, reduces a small portion of the ferric oxide to magnetite and so greatly enhances the susceptibility. Heated in a thin layer on a crucible lid it does not show this effect, or scarcely so. When it is remembered that one part of carbon can reduce eighty times its own weight of  $\text{Fe}_2\text{O}_3$  to  $\text{Fe}_3\text{O}_4$ , and that the susceptibility of magnetite is some 10,000 times greater than that of  $\text{Fe}_2\text{O}_3$ , the enormous error that can be introduced by traces of organic impurity will be realised. In fact, there is little doubt that the change in susceptibility brought about by heating pure  $\text{Fe}_2\text{O}_3$  with any substance capable of reducing it would be a more delicate test for, say, organic carbon or hydrogen than any other at present known.

Table II: Magnetic properties of material in bars

Substance	$H$ for $\mu_{\max}$	$\mu_{\max}$	$k_0$	Density	$k_m$	$H_c$	$B_{\text{rem}}$
<i>Experiments with bars of compressed powders</i>							
$\text{Fe}_3\text{O}_4$	207	3.50	0.198	1.73	0.115	49.2	248
$\text{Fe}_2\text{O}_3$ from oxidised $\text{Fe}_3\text{O}_4$	180	3.68	0.214	1.67	0.128	64.7	252
Lepidocrocite Easton	155	2.71	0.136	2.49	0.055	41.4	184
Lepidocrocite Siegen	180	2.47	0.117	2.27	0.0516	55	202
$\text{MgO} \cdot \text{Fe}_2\text{O}_3$	233	1.83	0.066	1.80	0.0367	39	87
$\text{CuO} \cdot \text{Fe}_2\text{O}_3$	155	5.37	0.348	3.02	0.115	54	324
Tilly Foster magnetite	103.5	4.39	0.27	2.84	0.095	25.9	114
Mineville magnetite	103	9.16	0.65	3.45	0.188	45	564
<i>Experiments with solid bars cut from magnetite</i>							
Tilly Foster	21	19.8	1.5	4.1	0.365	10.6	160
Mineville	55	35	2.7	5.12	0.527	20.7	1168

## § 5. COMPRESSED BARS

The modified Curie Balance previously described\* (in which an electromagnet enables the field strength to be varied through very wide limits) was used for the determination of the susceptibilities of all the oxides in the form of powder, and so long as the value of the susceptibility was not high and the retained magnetisation not large it proved entirely satisfactory; but when used for comparing substances of such high permeability as magnetite and ferromagnetic  $\text{Fe}_2\text{O}_3$  it was, on account of "end effect," unreliable, and tended to give too low values. Accordingly, the method was devised of moulding the powders into the form of rectangular bars 4 cm. long and 1 cm. by 1 cm. in a strong gunmetal mould, by mixing them into a stiff paste with some binding material (such as collodion, boiled starch, or a warm solution of photographic gelatine, which last was found on the whole the most satisfactory) and compressing them with a pressure of about 2 tons per square inch. After removal from the mould, which had removable sides held in position by bolts, they were allowed to dry in the air and finally introduced into the gap of a ring magnet, of which a full account has already been published†, where they formed an isthmus across the pole gap. Coils of fine wire wound on closely fitting formers of thin card or varnished paper were slipped over the specimens before insertion into the slots in the electromagnet. In this way the magnetic induction and permeability of the substances in the form of compact bars were obtained. Curves showing the relation between the permeability  $\mu$  and the magnetising force  $H$  are given in the diagram, and experimental data are given in Table II. The results justified our expectation by giving much higher values than could be obtained from the loose powders, and enabled readings for the force  $H$ , at which maximum permeability  $\mu$  occurred, to be recorded, and the apparent coercive

\* *Phil. Trans. R. S. A*, 219, Appendix (1919).† *Proc. Phys. Soc.* 31, 299-315 (1919).

force\*  $H_c$  and the retained magnetic induction  $B_{rem}$  to be measured in the usual way with a ring magnet. But we realise clearly that the values thus obtained are greatly influenced by the fact that the specimens still consist of particles, compressed, it is true, and held together with a binder, but not the solid material of which the powder consists. Comparison figures for bars moulded in this way out of powdered magnetite from both Tilly Foster and Mineville, N.Y. specimens with those obtained with bars cut from the solid material, are also given. The columns headed  $k_v$ ,  $k_m$  show respectively the volume and mass-susceptibility in c. g. s. units.

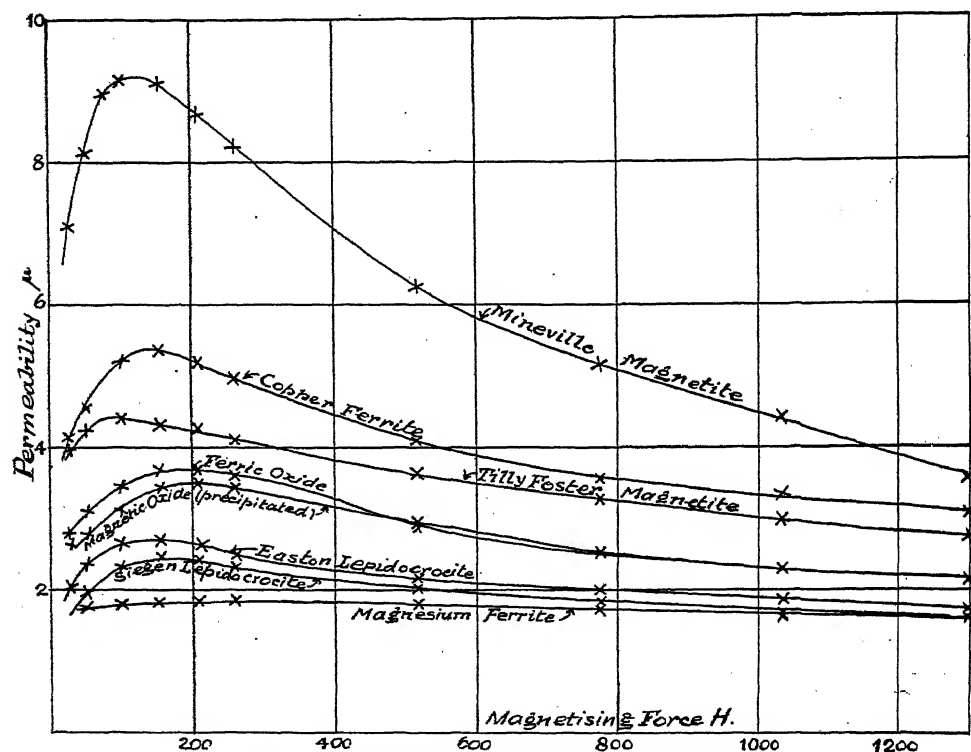


Fig. 1. Permeability curves of compressed powders.

It will be seen that results for the solid bars are between three and four times as great as for the bars of compressed powder, although the actual weight of dry binding material was only from 1 to 2 per cent. of the whole mass. The discontinuity in any such synthetic bar will naturally have a greater effect the higher the true permeability; hence it is believed that the values obtained in this way with the powders of lepidocrocite, artificial magnetic ferric oxide, etc. as detailed in Table II will be nearer their true values than with native magnetite. A comparison between powders and compressed bars has not been attempted on the grounds of the inequality in the corresponding magnetic forces employed.

\* This coercive force is that particular reverse force which reduces the magnetic induction,  $B$ , to zero and not the force which when removed leaves the specimen in a demagnetised state.

NOTE ADDED NOVEMBER 23, 1928

J. Huggett and G. Chaudron in a recent communication\* on magnetic sesquioxide of iron refer to it as having been discovered by Malaguti in 1863, whereas in fact the first recorded observation is that of Robbins four years earlier. They find a great difference in the thermal stability of the magnetic form according to whether it is prepared from commercial "pure ferric nitrate" or from the nitrate obtained by dissolving pure iron in nitric acid, recrystallising several times and then precipitating, washing and drying. After conversion into the magnetic form the product so obtained is transformed into the ordinary oxide by heating to  $350^{\circ}$ – $450^{\circ}$  C., while that from the "pure nitrate" requires to be heated to nearly  $700^{\circ}$  C. This difference they attribute to impurities. Their view may be correct, but it is difficult to see what impurities could be present in the commercial "pure nitrate" that could pass into the oxide and cause the difference in question.

We have found magnesia very potent in giving a high permanent susceptibility to ferric oxide, but even  $\text{MgO} \cdot \text{Fe}_2\text{O}_3$  containing about 20 per cent. of magnesia has only about a quarter of the susceptibility of ferromagnetic  $\text{Fe}_2\text{O}_3$ .

The curve given by Huggett and Chaudron shows the magnetisation of the oxide from the commercial nitrate to be higher on regaining room temperature after heating to  $650^{\circ}$  C. than it was initially.

They furnish no statement as to the magnitude of the magnetic field employed and the magnetisation is recorded as "deviation (cms.)": it is therefore impossible to obtain an approximate estimate of the susceptibility of the oxides with which they worked.

## DISCUSSION

THE PRESIDENT: The subject of the magnetic susceptibility of crystalline minerals is acquiring new interest from studies of their crystal lattice structure. On the utilisation of compressed powders I would suggest that a series of magnetic measurements might with advantage be made on the same powder at various dilutions in a neutral medium such as starch and then extrapolation might be attempted to obtain the values for zero dilution.

AUTHORS' reply: In connection with the suggestion made by the President we would refer to experiments on mixtures of powdered magnetite and crushed quartz in varying proportions which have been described by Sosman and Hostetter. In these experiments they measured the pull in a non-uniform field†. Auerbach‡ used reduced metallic iron and wood powder; E. Wilson§ examined iron filings alone and mixed with ferromanganese by a ring method.

\* *Comptes Rendus*, 186, 1617–19 (1928).

† Sosman and Hostetter, *Trans. Amer. Inst. of Mining Engineering*, No. 126, June 1917; Benedicks, *Journal Iron and Steel Institute*, 1914, pp. 407–459.

‡ *Wiedemann's Annalen*, 11, 353–394.

§ *The Electrician*, Oct. 5, 1900.

## DEMONSTRATIONS

Demonstration of a New Device for Thermostat Control, given by Mr H. F. T. JARVIS on October 28, 1928.

The device was designed to control the intermittent energisation of an immersion heater by which the temperature of a tank of water is kept constant. A large bulb full of toluol, immersed in the water, governs the level of a column of mercury on which floats a glass cylinder controlling two alternative wire-mercury contacts in circuit with solenoids which serve to rock in opposite directions a relay switch controlling the heating circuit. The relay switch comprises an evacuated bent glass tube containing a pool of mercury which connects a central wire terminal with one or other of two end terminals. By means of this arrangement a temperature constant within  $\frac{1}{50}^{\circ}$  C. was maintained for a fortnight. The temperature can be adjusted by varying the quantity of mercury in the controlling column. A full description and diagram of the apparatus will be found in the *Journal of Scientific Instruments*, 4, no. 10 (July 1927).

Demonstration of Emulsions showing Chromatic Effects, given by R. H. HUMPHRY, M.Sc., The Sir John Cass Technical Institute, on November 23, 1928.

The experiments shown were similar to those described by Holmes and Cameron\*. The refractive index of glycerol (1.467) lies between that of benzene (1.502) and that of acetone (1.359). A stable emulsion of glycerol in acetone may be made by using pyroxylin (1 to 2 per cent.) as the emulsifying agent; such emulsions are milky, the glycerol being the disperse phase. By addition of benzene, which mixes with the acetone, the refractive index of the dispersion medium may be varied continuously and, when it is equal to that of the disperse phase, the emulsion becomes clear. Owing, however, to the large optical dispersion of the medium as compared with glycerol, equality of refractive index is only possible for light of a particular wave-length and, if the emulsion is viewed in white light, the transmitted light is of this particular region of the spectrum. Light of other wave-lengths suffers innumerable refractions and appears as scattered light of a colour complementary to that transmitted. The variation which is made by addition of benzene causes the transmitted light to change from violet, through the spectrum to orange, with corresponding change in the complementary colour. Subsequent addition of the other component (acetone) effects a colour change in the reverse direction. A series of emulsions exhibiting these chromatic effects was prepared and shown.

The effect of changing the temperature of such an emulsion was also demonstrated; a change of  $1^{\circ}$  C. causes a perceptible alteration of the colour, the change being, for a fall in temperature, in the same direction as for increasing proportion of benzene.

\* *Journ. Amer. Chem. Soc.* 44, 71 (1922).

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## THE MEASUREMENT OF THE ANODE CIRCUIT IMPEDANCES AND MUTUAL CONDUCTANCES OF THERMIONIC VALVES

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**ABSTRACT.** The paper describes the application of the Wheatstone Bridge to the measurement of the anode circuit admittance or impedance, and the mutual conductance of a valve under actual operating conditions. Current of telephonic frequency is used. The measurements can be made for grid bias of any desired value, and both methods can be made direct-reading. The results of measurements made on a few typical valves are given, and it is shown that although both anode circuit resistance and mutual conductance vary very considerably with the grid bias, the product of the two, which gives the voltage factor of the valve, is approximately constant. The anode circuit admittance consists of a conductance associated with a comparatively small capacity, but this capacity is larger than the inter-electrode capacities of the valve when the filament is cold. The increase in the effective values of the inter-electrode capacities is explained by the presence of the space charge, which also has the effects of making these capacities vary with the frequency and of giving them a comparatively high power factor, especially at low frequencies.

### § 1. INTRODUCTION

VARIOUS methods of measuring the characteristic constants of thermionic valves have already been described\*. Approximate values may be obtained from the static characteristic curves, but in order to obtain values under actual working conditions, alternating current must be used. For precision measurements at telephonic frequencies, circuits of the Wheatstone bridge type have much to recommend them. With proper technique, errors due to earth capacities can be successfully avoided even at high frequencies, and in this respect they are preferred by the author to the various alternating current methods of the potentiometer type which have already been described for the measurement of the constants of

\* See for example Van der Bijl, *The Thermionic Vacuum Tube*, pp. 197-205; Eccles, *Continuous Wave Wireless Telegraphy*, pp. 386-393.

valves. The present paper describes the application of this network to the measurement of the mutual conductances and anode circuit impedances of thermionic valves.

In considering the behaviour of the valve with respect to alternating current, we may regard it as a device with three terminals—the anode  $A$ , the grid  $G$ , and the filament  $F$ , Fig. 1. A current  $i_g$  (the “grid current”) is passed through the valve by way of the terminals  $G$  and  $F$ , and a current  $I_a$  (the “anode current”) is taken from it by way of the terminals  $A$  and  $F$ . Let  $v$  be the p.d. between  $G$  and  $F$ , and  $V$  that between  $A$  and  $F$ . Then the important characteristic constants are:

- (a) The grid circuit admittance, or input admittance  $\partial i_g / \partial v$ .
- (b) The anode circuit admittance, or output admittance  $\partial I_a / \partial V$ .
- (c) The mutual admittance  $\partial I_a / \partial v$ .

The reciprocals of these give the corresponding impedances.

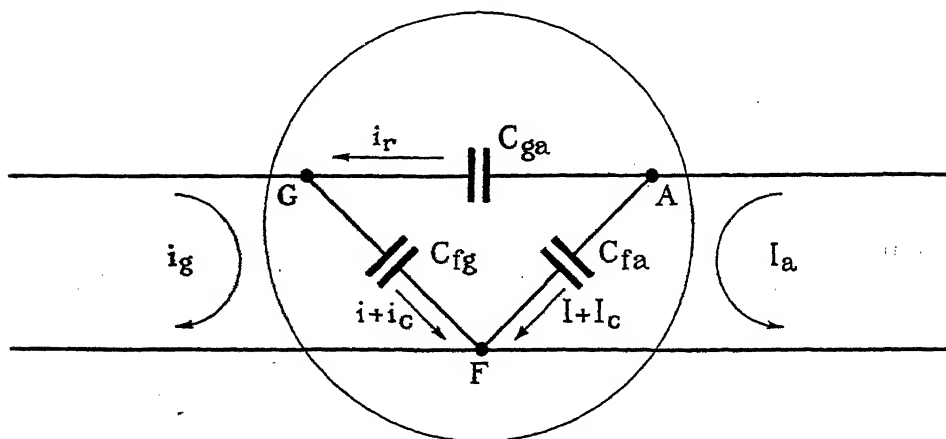


Fig. 1. Schematic diagram of valve.

These quantities are nearly but not quite pure conductances. The actual current between the valve electrodes is partly thermionic ( $i$  and  $I$ ) and partly capacity current ( $i_c$ ,  $I_c$ , and  $i_r$ , Fig. 1), and by a simple application of Kirchhoff's Laws to Fig. 1 it may be shown that in the usual vector notation

$$\partial i_g / \partial v = \partial i / \partial v + j\omega (C_{fg} + C_{ga}) = \partial i / \partial v + j\omega C_g \quad \dots\dots(1),$$

$$\partial I_a / \partial V = \partial I / \partial V + j\omega (C_{fa} + C_{ga}) = \partial I / \partial V + j\omega C_a \quad \dots\dots(2),$$

$$\partial I_a / \partial v = \partial I / \partial v - j\omega C_{ga} \quad \dots\dots(3),$$

where  $C_{fg}$ ,  $C_{ga}$ ,  $C_{fa}$  are the inter-electrode capacities of the valve as shown in Fig. 1.  $C_g$  may be termed the grid circuit capacity, or input capacity of the valve, and  $C_a$  its output capacity, or anode circuit capacity.

Thus each of the above admittances contains a conductance term and a quadrature term. The measurement of the input admittance  $\partial i_g / \partial v$  has been described in a previous paper\*. The present paper is concerned with  $\partial I_a / \partial V$  and  $\partial I / \partial v$ .

\* Hartshorn, *Proc. Phys. Soc.* 39, 108 (1927).

## § 2. THE MEASUREMENT OF ANODE CIRCUIT IMPEDANCE

The application of the Wheatstone network to the measurement of the anode circuit impedance of a valve is fairly straightforward. Circuits for comparatively rough measurements of anode circuit resistance have been described by Barkhausen\* and Bagally†, but for precision work and especially if the actual impedance or admittance is required, and not merely the resistance, a number of refinements are necessary. The actual arrangement used by the author for accurate measurements is shown in Fig. 2. The bridge proper is the network *DBCF*, the valve being connected in the arm *FD* by means of the filament and anode. The other three arms consist of non-inductive resistances  $R_1$ ,  $R_2$ , and  $R_3$ , the last being shunted

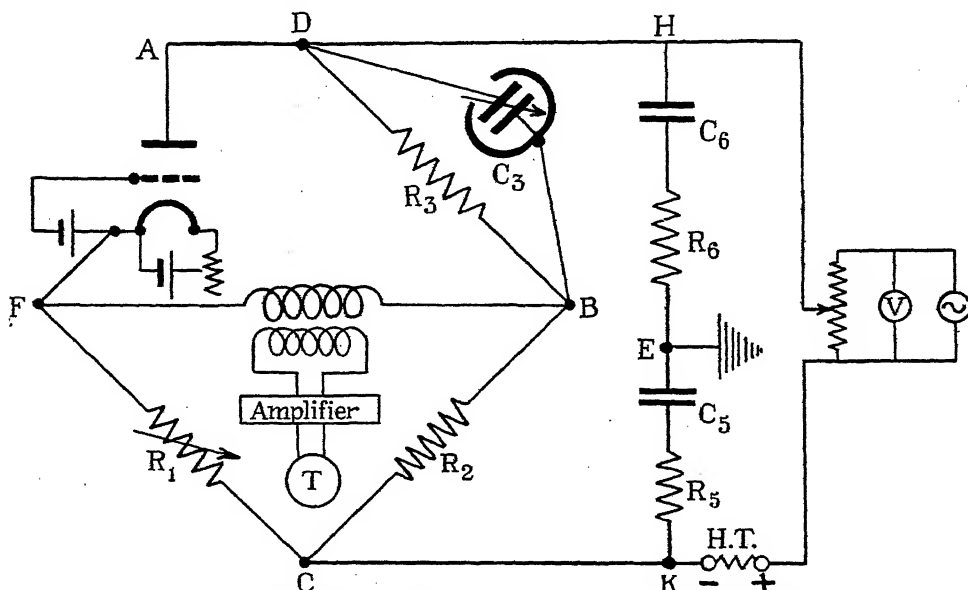


Fig. 2. Bridge for the measurement of anode circuit impedance.

by a small shielded variable air condenser  $C_3$ . A potential difference of telephonic frequency, which could be varied in magnitude from 0.2 volt to 20 volts, was applied to the points *D* and *C*, and a detector of alternating current consisting of a telephone receiver, with or without an amplifier, was applied to the points *F* and *B*.

The current flowing in the arm *FD* of the bridge is  $I_a$ , the anode current, and the voltage across it is  $V$ , the anode voltage. If  $\delta I_a$  and  $\delta V$  are the amplitudes of the alternating components of these quantities, then the effective impedance of the arm *FD* is  $\delta V / \delta I_a$ , and when the detector *FB* is silent, i.e., the bridge is balanced for the alternating components of current and voltage, it is evident that the equation for balance is

$$\frac{\delta I_a}{\delta V} = \frac{R_2}{R_1} \left[ \frac{1}{R_3} + j\omega C_3 \right] \quad \dots\dots(4).$$

\* Barkhausen, *Jahrbuch der drahtlosen Telegr.* 14, 36 (1919).

† Bagally, *Journ. Sci. Instr.* 4, 46 (1926).



Since the grid voltage  $v$  is maintained constant, if the applied voltage be reduced until the bridge readings become independent of the applied voltage, they then give the value of  $\partial I_a / \partial V$  the anode circuit admittance. The two components of this are given by (see equation (2)):

$$\frac{\partial I}{\partial V} = \frac{R_2}{R_1} \cdot \frac{1}{R_3} \quad \dots\dots(5),$$

$$j\omega C_a = j\omega C_3 \cdot R_2 / R_1 \quad \dots\dots(6).$$

For accuracy the choice of suitable values for the various bridge components is important. Those used were  $R_3 = 10,000$  ohms,  $R_2 = 100$  or  $1000$  ohms depending on the valve to be tested.  $R_1$  was a resistance box giving  $1000$  ohms in steps of  $0.1$  ohm, and  $C_3$  had a maximum value of about  $200 \mu\text{F}$ . These resistances were completely shielded, the shields being connected to earth. A Wagner\* earthing device  $HK$  was applied to the bridge, so as to maintain the points  $F$  and  $B$  at earth potential. Thus errors due to the comparatively large earth capacities of the filament and grid bias batteries are completely avoided. To increase the stability of the circuit the arm  $HK$  should be preferably of low impedance, say  $R_5 = 100$  ohms,  $R_6 = 1000$  ohms,  $C_5 = 1 \mu\text{F}$ ,  $C_6 = 10 \mu\text{F}$ . These condensers are to prevent the h.t. battery from discharging through the resistances  $R_5$  and  $R_6$ .

The h.t. battery lies outside the bridge, so that its resistance and earth capacity do not affect the balance point. Two sources of error remain to be considered:

(a) Stray magnetic coupling between the detector circuit and the a.c. supply circuit. This is allowed for by including reversing switches in the detector and supply circuits, and taking readings for the four possible relative positions of these switches, and averaging them. The total deviation of any reading from the mean is usually small.

(b) Residual inductance in the coils  $R_1$ ,  $R_2$  and  $R_3$ . These residual inductances were measured and suitable corrections applied.

Balance was obtained by varying  $R_1$  and  $C_3$ . When the minimum value of the condenser  $C_3$  was not small enough to give balance, another condenser was connected across  $R_2$ . It is easy to show that the complete equation for the capacity  $C_a$  takes the form

$$C_a = \frac{R_2}{R_1} C_3 - \frac{R_2^2}{R_1 R_3} \cdot C_2 + \frac{R_2}{R_1 R_3} (\tau_2 - \tau_1 - \tau_3) \quad \dots\dots(7),$$

$\tau_1$ ,  $\tau_2$  and  $\tau_3$  being the time constants, or quotients of residual inductance and resistance, of the coils  $R_1$ ,  $R_2$  and  $R_3$  respectively.

### Results

Measurements of anode circuit impedance were made by this method on four typical valves. The results, which are given in Table 1, are expressed by stating the equivalent anode circuit capacity  $C_a$ , and  $R_a$ , the reciprocal of the anode circuit conductance  $\partial I / \partial V$  as defined by (2). This may be defined as the anode circuit resistance†.

\* K. W. Wagner, *E.T.Z.* 40, 1001 (1911).

† Sometimes  $\partial V / \partial I$  is regarded as the anode circuit resistance,  $V$  being considered as a function of the two currents  $I$  and  $i$ . This gives a value slightly different from that given by the above definition, but the difference is of no great practical importance. See for example Nichols, *Phys. Rev.* 13, 411 (1919).

The results exhibit a number of interesting features. Measurements were made at frequencies of 1000, 2000, and 4000 cycles per second, but the anode circuit resistance was practically the same at all these frequencies. The actual changes shown in Table 1 were found to be due, not to the change of frequency, but either to a change in the thermionic emission of the filament with time (such changes were always very rapid when the filament current was first switched on, but gradually became slower) or to a change in the value of  $\delta V/\delta I_a$  owing to the curvature of the characteristic curve of the valve. This curvature was appreciable in every case. It caused the first harmonic to be audible in the telephone even when the bridge was perfectly balanced for the fundamental, whereas if a wire wound resistance were substituted for the valve, this harmonic disappeared.

Table 1. The anode circuit resistance and capacity of various valves

Valve	Frequency, cycles per sec.	$R_a$ (ohms)	$C_a$ filament emitting ( $\mu\mu\text{F}$ )	$C_a$ filament cold ( $\mu\mu\text{F}$ )
P.M. 1 A Anode voltage: 100 Fil. voltage: 2 Grid bias: zero	1000	77,260	17.3	13.2
	2000	77,340	16.4	12.7
	4000	77,300	16.0	12.5
D.E.R. Anode voltage: 80 Fil. voltage: 2 Grid bias: - 2	1000	19,090	16.5	8.6
	2000	19,120	14.5	8.3
	4000	19,180	14	7.8
	6000	19,190	13.5	8
P.M. 252 Anode voltage: 100 Fil. voltage: 2 Grid bias: - 10	1000	3,935	21.5	14.0
	2000	3,934	18	13.8
	4000	3,932	16	13.8
R. Anode voltage: 100 Fil. voltage: 4 Grid bias: zero	1000	27,700	35.0	20.8
	2000	27,700	27.5	18.5
	4000	27,600	24.5	17

The equivalent anode circuit capacity  $C_a$  is by no means independent of the frequency. In the case of the P.M. 252 valve,  $C_a$  at 1000 ~ is 30 per cent. greater than it is at 4000 ~. The change is rather less in other cases, but in every case the equivalent anode circuit capacity decreases with increase of frequency.

The last column of Table 1 gives the values of the anode circuit capacity when the filament current was switched off. It consists of the sum of the two capacities  $C_{fa}$  and  $C_{ga}$  together with the capacities of connecting leads, etc. It was measured on the same bridge, without in any way disturbing the leads or batteries. On switching off the filament current a standard resistance of approximately the same value as the anode circuit resistance of the valve was connected across  $FD$  (Fig. 2), so that when balance was again obtained the conditions were as nearly as possible the same as in the first instance. It is to be noted that, in every case, the effective anode circuit capacity, when the thermionic current is flowing, is greater than the capacity of the same circuit when the filament is cold. Moreover, this capacity with

the filament cold is sometimes very nearly independent of the frequency, whereas the capacity with the filament glowing always varies with the frequency.

The explanation of these facts is to be found in the presence of the space charge between the filament and the anode. The free electrons constituting this charge endow this space with a certain conductivity which is not uniform, but is greatest near the surface of the filament, and decreases as we approach the anode. In other words, the filament regarded as a conducting electrode is increased in size by the space charge (its boundary becoming indefinite) and the filament-anode capacity is therefore increased.

Approaching the matter from another point of view, if  $\epsilon$  is the dielectric constant of the medium at any point between filament and anode, and  $\sigma$  is the conductivity at this point due to the free electrons, then it is evident that the quotient  $\epsilon/\sigma$  will vary from point to point as we pass from filament to anode. The space, therefore, possesses the properties postulated by Maxwell\* in his theory of dielectric absorption, and the mathematical development of this theory shows that the following phenomena are a necessary consequence of this property:

(a) The capacity between the filament and anode must be greater than their "geometrical mutual capacity," which is practically the same as the capacity when the filament is cold.

(b) The increase in capacity will vary with the frequency, being greatest at low frequencies, and gradually approaching zero at very high frequencies.

(c) The conductance between filament and anode when alternating voltage is applied will be greater than the conductance with constant applied voltage, i.e. the "static" value. The a.c. conductance will increase as the frequency increases from zero, approaching a constant value at high frequencies.

This provides a complete explanation of the capacity values given above. The change in conductance with frequency was not actually observed. It is evidently very small in amount, and was masked by variations due to other causes, but it is interesting to note that the resistance of a valve as determined from the characteristic curves must be slightly different from the dynamic value, or value determined by a.c. methods, the a.c. resistance being the smaller.

The alternating current conductance due to the space charge is best measured by a measurement of input impedance, in which case this conductance forms a large part of the total conductance, and is therefore not likely to be masked by other effects. The results given in a previous paper† show the effect quite clearly, though their significance was not fully realised at the time. The input capacity of an R. valve was found to be  $13.0\mu\text{F}$ , with a power factor of 0.21 at 1000 cycles per second when the filament was cold. On the application of full voltage to the filament, the capacity rose to  $14.6\mu\text{F}$ , and the power factor became as high as 0.38. The increase of power factor is attributed to a grid circuit conductance (0.015 micro-mho), due to the space charge. This conductance existed even when negative grid bias was used. An important conclusion is that the inter-electrode capacities of a valve

\* Maxwell, *Electricity and Magnetism*, 1, 328; Hartshorn, *I.E.E. Journal*, 64, 1152 (1926).

† Hartshorn, *Proc. Phys. Soc.* 39, 114 (1927).

must be regarded as having comparatively high power factors at audio frequencies when the valve is working, even if measurements made when the filament is cold give very low power factors. The space charge may give rise to alternating current conductance even under conditions under which no d.c. conductance is detectable. The power factor due to the space charge will be greatest at low frequencies, gradually decreasing as the frequency is raised, as in the case of a non-homogeneous dielectric\*.

### § 3. THE MEASUREMENT OF MUTUAL CONDUCTANCE

Fig. 3 shows the Wheatstone Bridge network arranged for the measurement of the mutual conductance of a valve.  $R_1$ ,  $R_2$ ,  $R_3$  are non-inductive resistances as in the previous case and  $C_3$  is a small variable air condenser. The valve is connected in the fourth arm by means of the grid and filament, the anode being connected

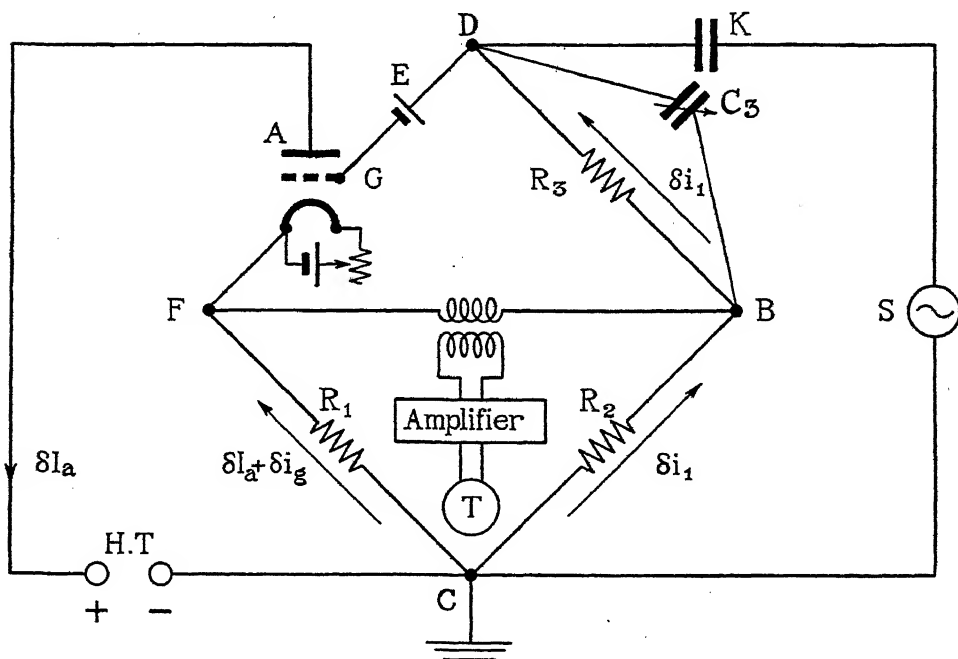


Fig. 3. Bridge for the measurement of mutual admittance.

through the h.t. battery to the point C. The source of telephonic frequency current and the detector of balance are the same as in the previous case, except that the applied voltage may be smaller, say 0.02 volt, if an amplifier is used in the detector circuit. The mean potential of the grid with respect to the filament is adjusted to any desired value by placing a "grid bias" battery  $E$  in series with the grid as shown in the diagram.

\* Hartshorn, *I.E.E. Journal*, 64, 1152 (1926).

In carrying out the measurements described later, bridge components of the following values were used,  $R_1 = R_2 = 100$  ohms,  $R_3 =$  a resistance box giving 10,000 ohms total, continuously variable,  $C_3 = 200 \mu\mu\text{F}$  maximum. The bridge was balanced with respect to alternating current by varying  $R_3$  and  $C_3$  until the telephone became silent.

Since the telephone detector responds only to variations of current or voltage, in deriving the equations of balance we need only consider the alternating components  $\delta i_g$ ,  $\delta I_a$ ,  $\delta v$ , and  $\delta V$ , of the grid current, anode current, grid voltage, and anode voltage respectively. When the bridge is balanced, there is no alternating current in  $FB$ . Thus the current flowing from  $C$  to  $F$  will be equal to the sum of those flowing from  $F$  to  $G$ , and from  $F$  to  $A$ , i.e.  $\delta i_g + \delta I_a$ . Let  $\delta i_1$  be the alternating current in the arms  $CB$  and  $BD$ . Then remembering that the alternating p.d. across the arm  $FD$  is  $\delta v$ , it is evident that the conditions of balance are

$$R_1 (\delta i_g + \delta I_a) = R_2 \cdot \delta i_1 \quad \dots\dots(8)$$

$$\text{and} \quad \delta v = Z_3 \cdot \delta i_1 \quad \dots\dots(9),$$

$$\text{where} \quad 1/Z_3 = 1/R_3 + j\omega C_3 \quad \dots\dots(10).$$

$$\text{Dividing (8) by (9), we have} \quad \frac{\delta i_g}{\delta v} + \frac{\delta I_a}{\delta v} = \frac{R_2}{R_1} \cdot \frac{1}{Z_3} \quad \dots\dots(11).$$

It should be noticed that the load in the anode circuit of the valve consists of the h.t. battery of resistance  $R_b$  say, in series with  $R_1$ . If  $R_1 + R_b$  be made small compared with the anode circuit resistance of the valve, the anode potential  $V$  will be approximately constant, and if in addition the applied voltage is very small equation (11) may be written with sufficient approximation

$$\frac{\partial i_g}{\partial v} + \frac{\partial I_a}{\partial v} = \frac{R_2}{R_1} \cdot \frac{1}{Z_3} = \frac{R_2}{R_1} \left[ \frac{1}{R_3} + j\omega C_3 \right].$$

Substituting equations (1) and (3) in this, we find

$$\frac{\partial i}{\partial v} + \frac{\partial I}{\partial v} + j\omega C_{fg} = \frac{R_2}{R_1} \left[ \frac{1}{R_3} + j\omega C_3 \right].$$

Equating the real terms of this expression and remembering that the grid conductance  $\partial i/\partial v$  is sensibly zero in most practical cases, we have the working equation for mutual conductance measurements

$$\frac{\partial I}{\partial v} = \frac{R_2}{R_1} \cdot \frac{1}{R_3} \quad \dots\dots(12).$$

In precision measurements it is sometimes necessary to apply a correction for the small variation of anode voltage. This variation is given by

$$\delta I_a R_b + (\delta I_a + \delta i_g) R_1 \quad \text{or} \quad (R_1 + R_b) \delta I_a,$$

the remaining term being negligible.

$$\text{Now} \quad \delta I_a = \frac{\partial I_a}{\partial v} \cdot \delta v + \frac{\partial I_a}{\partial V} \delta V \quad (\text{approximately})$$

$$\text{or} \quad \delta I_a \doteq \frac{\partial I_a}{\partial v} \cdot \delta v + \frac{R_1 + R_b}{R_a} \delta I_a$$

$$\text{since} \quad \frac{\partial I_a}{\partial V} \doteq \frac{\partial I}{\partial V} = \frac{1}{R_a},$$

$$\therefore \frac{\partial I_a}{\partial v} = \frac{\delta I_a}{\delta v} \left[ 1 - \frac{R_1 + R_b}{R_a} \right] \quad \dots\dots(13).$$

The term in brackets is therefore the required correction factor, and equation (12) is replaced by the more accurate equation

$$\frac{\partial I}{\partial v} = \frac{R_2}{R_1} \cdot \frac{1}{R_3} \left[ 1 - \frac{R_1 + R_b}{R_a} \right] \quad \dots\dots(14).$$

In order to obtain the actual value of the mean potential of the grid with respect to that of the "zero" end of the filament, i.e. the "grid bias," the values of the constant components of the currents and voltages must be considered. The constant component of the anode current  $I$  flows from  $C$  to  $F$ , partly by way of  $R_1$ , and partly by way of the path  $CBF$ . Thus there is a constant current in the detector arm  $BF$ , and the bridge is therefore not balanced as regards the constant components of current and voltage. A condenser  $K$  is placed in series with the source of alternating current  $S$ . This prevents any constant current flowing from  $D$  to  $B$  via  $S$ , and at the same time allows the passage of alternating current. A condenser of  $0.5 \mu F$  was used for  $K$ , but it could be much less. Owing to the very high resistance of the grid circuit of the valve, the constant current in the bridge arms  $DF$  and  $DB$  is very small. The mean potential of  $D$  is therefore practically the same as that of  $B$ , and if  $E$  is the e.m.f. of the battery  $E$ , and  $e$  is the p.d. between  $B$  and  $F$ , the "grid bias" or the p.d. between  $G$  and  $F$  is  $(E + e)$ . The value of  $e$  may easily be calculated, if the total anode current  $I$  and also the d.c. resistances of  $FB$ ,  $R_1$ , and  $R_2$  are known, but it is more convenient to use a transformer with a low resistance primary winding  $FB$  to couple the bridge to the amplifier. In this way  $e$  can be made negligibly small, so that the grid bias is given simply by  $E$ . Since the resistance of the grid bias battery is included in the measurements, it should be as small as possible, i.e. an accumulator should be used, but in doubtful cases the resistance of this battery can always be eliminated by taking an additional reading with the battery transferred to the arm  $DB$ . The grid bias is unaltered, and the mean of the two readings will give the true value of the mutual conductance. It is also possible to work with the grid bias battery in the detector arm  $FB$ , and so remove it from the bridge arms proper. This arrangement was used for some measurements, but it is considered to be not quite so convenient as the one shown in Fig. 3.

When the quadrature component of the admittance is not required, it is not necessary to use a Wagner earth. Sufficient accuracy is obtained by earthing the

point  $C$ , at the same time making the resistances  $R_1$  and  $R_2$  as small as possible (100 ohms or even 10 ohms). This ensures that the detector arm  $FB$  is not much above earth potential. The same applies to the measurement of anode circuit resistance.

The thermionic current  $I$  is usually expressed as a function of the single variable  $(V + \mu v + c)$ , where  $\mu$  is the "voltage factor" of the valve:

$$I = F(V + \mu v + c) \quad \dots\dots(15).$$

It follows that

$$\partial I / \partial v = \mu \cdot \partial I / \partial V \quad \dots\dots(16).$$

Thus the product of the anode circuit resistance  $R_a$ , and mutual conductance  $G_m$ , of a valve at any operating point  $(V, v)$  gives the value of  $\mu$ .

With the simple earthing arrangement, values of both  $R_a$  and  $G_m$  can be obtained very quickly over the whole working range of grid bias.

### Results

Measurements were made in this way on a few typical valves. The values of  $R_a$  and  $G_m$  are given in the third and fourth columns of Table 2. Their product ( $\mu$ ) is given in the last column. It is to be noted that although the values of  $R_a$  and  $G_m$  vary considerably with variations of grid bias, the product is very nearly constant. The variations in the values of  $\mu$  in Table 2 show with what accuracy this may be regarded as a true constant for any one valve.

With regard to the accuracy of the measurements, a number of factors have to be considered besides mere sensitivity. The sensitivity was in all cases greater than 0.1 per cent., using an input p.d. of 0.02 volt for the mutual conductance and 0.2 volt for the anode circuit resistance measurements, but the properties of the valves were found to vary appreciably with time of application of the various voltages. In the case of S.P. 18 R.R. valve, a change of about 10 per cent. was liable to occur in 10 minutes, but after a time the valve appeared to settle down, although irregular fluctuations of 2 or 3 per cent. always occurred. The other valves were much more stable, and the values of  $G_m$  and  $R_a$  are probably trustworthy to about 0.2 per cent. in most cases.

An examination of the results for  $R_a$  and  $G_m$  for various values of grid bias shows that the characteristic curves of the valves cannot be regarded as really straight even over the usual working portion. Very considerable changes of slope occur from point to point, and it is evident that no single value of anode circuit resistance can be assigned to any valve with an accuracy greater than 10 per cent. unless all the operating voltages are specified.

The values of  $1/R_a$  and  $G_m$  may be regarded as the slopes of tangents to the characteristic curves at the operating point, and in order to determine these it is, strictly speaking, necessary to use indefinitely small applied voltages. The bridges actually measure the slopes of two chords instead of tangents, since the applied voltage is necessarily finite. When using applied voltages of the order 0.1, errors due to this are usually negligible, e.g. doubling the applied voltage caused no

appreciable change of bridge reading in general, but when the operating point ( $V, v$ ) is near the bend of the characteristic curve, particular attention must be paid to this point, especially when  $\mu$  is to be determined from the product  $G_m R_a$ . A consideration of equation (15) will show that  $\mu$  will be correctly given by the effective values of  $G_m$  and  $R_a$  even when the applied alternating voltage ( $\delta V$  or  $\delta v$ ) is not very small, provided that  $\delta V/\delta v = \mu$ . It was on this account that the applied voltage for the  $G_m$  measurements was roughly one-tenth of that used for the  $R_a$  measurements.

Table 2. Measured values of mutual conductance ( $G_m$ ), anode circuit resistance ( $R_a$ ), and voltage factor ( $\mu$ ) of typical valves

Valve	Grid bias voltage	$R_a$ (ohms)	Mutual conductance ( $G_m$ ) micro-mhos	Voltage factor ( $\mu$ )
P.M. 1 L.F. Fil. voltage: 2.0 Anode voltage: 100	+ 4	10,370	797	8.2 <sub>6</sub>
	+ 2	10,400	828	8.6 <sub>1</sub>
	0	10,630	820	8.7 <sub>2</sub>
	- 2	11,280	770	8.6 <sub>9</sub>
	- 4	12,410	701	8.7 <sub>0</sub>
	- 6	14,720	593	8.7 <sub>3</sub>
P.M. 1 H.F. Fil. voltage: 2.0 Anode voltage: 80	+ 4	17,020	992	16.8 <sub>9</sub>
	+ 2	18,940	910	17.2 <sub>3</sub>
	0	22,520	762	17.1 <sub>8</sub>
	- 2	32,810	524	17.2 <sub>0</sub>
	- 4	151,200	108.0	16.3 <sub>3</sub>
D.E.H. Fil. voltage: 2.0 Anode voltage: 150	+ 2	54,630	757	41.3
	0	71,100	575	40.9
	- 2	156,700	248.4	38.9
D.E.R. Fil. voltage: 2.0 Anode voltage: 80	+ 4	20,200	539	10.9
	+ 2	21,680	514	11.1
	0	24,310	451	11.0
	- 2	28,830	355	10.2
	- 4	37,480	253.9	9.5
S.P. 18 R.R. Fil. voltage: 1.6 Anode voltage: 100	+ 4	3,730	1727	6.4 <sub>4</sub>
	+ 2	3,960	1800	7.1 <sub>2</sub>
	0	4,055	1669	6.7 <sub>8</sub>
	- 2	4,440	1550	6.8 <sub>9</sub>
	- 4	4,617	1386	6.4 <sub>0</sub>
	- 6	5,100	1191	6.0 <sub>8</sub>
R.C. 2 Fil. voltage: 2.0 Anode voltage: 100	- 1	338,000	135	45.6
	- 2	512,000	85	43.6

## DISCUSSION

Dr J. H. VINCENT: These experiments of Mr Hartshorn are of great use as well as elegance. The results are fortunately not revolutionary. In particular it is a comfort to be assured that the voltage factor measured by his methods remains sensibly constant.



Mr A. G. WARREN: In view of increase of inter-electrode capacity due to space charge, it would appear that values  $C_a$ ,  $C_g$  etc. would be functions of grid voltage. Has the author noted any greater increase in filament/anode capacity for a gettered valve than for one which is not gettered? One would anticipate that the presence of a conducting internal coating on the glass, which naturally tends to assume cathode potential when the filament is lighted, would increase the effective filament/anode capacity.

Mr W. E. BENHAM: I should like to endorse the last speaker's remarks concerning the variation of capacity with voltage. It would appear that there is a term of the form  $v \partial C / \partial v$  missing from equations (1) to (3). As a result of some experiments on valve capacities I came to the conclusion that the self capacity of a triode could be expressed approximately by the equation

$$C = C_0 (1 + A/R_a),$$

where  $A$  is constant for a given anode voltage (120 volts) and equal to about  $6 \times 10^3$ ,  $R_a$  being the anode slope resistance in ohms. The measurements were made on Osram D.E.P. 215 and D.E.H.L. 210 type valves at a frequency as high as  $5 \times 10^6$  cycles per second, using a resonance method incapable of high precision.

The author's conclusions as to the increase of valve capacity (at telephonic frequencies) due to space-charge are of great interest, and are in qualitative agreement with a calculation giving  $C = \frac{2}{3} C_0$  for zero frequency. The author's experimental method should be capable of yielding accurate results over a wide range of frequencies, but until a correction is made I think his figures for the output capacity and its frequency-variation must be accepted with reserve. Another consideration presenting difficulties is the influence of traces of ionization.

AUTHOR'S reply: I agree with Mr Warren that the effective values of the valve capacities are functions of the grid voltage,  $v$ . Indeed, I consider that one of the most important conclusions to be drawn from my investigation is that the effective inter-electrode capacities of valves are not simply the same as the corresponding "static" capacities, but that they vary with the position on the characteristic curve of the operating point ( $V, v$ ), and therefore the resistance of the valve, and also with the frequency. My results show the kind of variation and its order of magnitude. I have not made comparative measurements on valves gettered and not gettered.

Mr Benham's suggestion that there is a term of the form  $v \partial C / \partial v$  missing from equations (1) to (3) is probably due to a misunderstanding of the nature of these equations. They must be regarded as *defining* the conductances and capacities measured by the bridge circuits. In each case they give the two quadrature components of a vector, and indicate their relationship to the three valve electrodes. Each equation applies at any one operating point ( $V, v$ ) and the values of the terms are, of course, quite different at different operating points. One must realize that the electrical path between any two valve electrodes is neither a conductor nor an insulator, and that the terms conductance and capacity can only be applied

in accordance with some arbitrary convention. Equations (1) to (3) express the convention used most widely in the study of imperfect dielectrics, and in electrical measurements generally. The introduction of another term would imply a different convention, and one inconsistent with general practice. On this understanding, there can be no question of correcting the results of the bridge measurements, and the presence of traces of ionization or any deposit on the "pinch" of the valve will cause no difficulty. They will affect the value of the capacity, but the bridge will measure the actual capacity under the working conditions.

I have made calculations of  $C/C_0$  at zero frequency, and agree with Mr Benham's value of  $\frac{4}{3}$  for the case of plane electrodes, and with Langmuir's theoretical formula for the thermionic current. This is, however, not a very practical case. My calculations show that the value of  $C/C_0$  depends greatly on the form of the filament, and on the actual formula used for the thermionic current. Taking various cases, values ranging from 1 to 2 or even greater can be obtained for  $C/C_0$  at zero frequency. In this connection, I presume that the constant  $A$  in Mr Benham's equation  $C/C_0 = 1 + A/R_a$  refers only to electrodes of one particular form. However, bearing in mind that the effect must be smaller at the higher frequencies, there does not seem much possibility of getting trustworthy results at radio frequencies, unless a high precision method be used, and in particular unless all stray earth-capacity effects be eliminated. The method I have described could, of course, be used at high frequencies, provided that suitable bridge components were used and that everything were properly screened. The practical difficulties would be considerable, but not insuperable.

# A METHOD FOR THE DETERMINATION OF THE EQUIVALENT RESISTANCE OF AIR-CONDENSERS AT HIGH FREQUENCIES

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**ABSTRACT.** The losses in air-condensers are divided into two portions, (1) those due to leakage through the solid dielectric, and (2) those due to terminal and plate resistance. A method is developed for measuring each, under conditions such that the other is negligibly small. The limits of the errors to which the methods are liable are discussed and some results of practical measurements are quoted.

THE losses in air-condensers such as are used in medium and high-frequency a.c. measurements may be safely assumed to arise from two sources, (1) Losses in the solid dielectric essential to the mechanical construction, and (2) The resistance of the leads from the terminals to the plates and of the plates themselves.

## § 1. LOSSES IN THE SOLID DIELECTRIC

The paths along which the first of these losses occur are limited to portions of solid dielectric between the terminals, pillars, etc., and the partial capacities due to flux along these paths form only a small portion of the total effective capacity, even at the minimum setting of a variable air-condenser. Consequently a high non-inductive resistance in parallel with a perfect condenser may, so far as such losses are concerned, be safely considered an equivalent circuit at any given frequency. The measurement with fair accuracy of the equivalent parallel resistance offers little difficulty.

A suitable circuit arrangement is shown in Fig. 1, in which  $C_1$  is the condenser under examination and  $C_2$  a second variable condenser of good construction and of about  $750\mu\text{F}$  capacity.  $C_1$  is set at its minimum reading, which will usually be of the order of  $50\mu\text{F}$  or less. For any given frequency the coil  $L$  should be chosen so that it is necessary to set  $C_2$  at about  $500\mu\text{F}$  for resonance.

On switching  $C_1$  out of circuit by the small link  $S$  the alteration of the  $C_2$  necessary to restore resonance will be only 10 per cent. or so of its actual value, and it may be assumed that the change of resistance of  $C_2$  due to the alteration is negligibly small. The lead resistance of  $C_1$  when set at its minimum value will, in a good condenser, be quite small compared with the series resistance equivalent to its solid insulation losses. Consequently the change of resistance of the tuned circuit on removing  $S$  may be assumed to be equivalent to these insulation losses

and may be readily measured with the aid of the voltmeter and the resistance substitution method. The results of measurements which show the above assumptions to be permissible are given later. (See Tables 1 and 4.)

## § 2. RESISTANCE OF THE LEADS AND PLATES

The similarity of the distribution of the lines of current-flow between two electrodes immersed in a conducting solution and of the lines of electric force between two insulated and charged surfaces of the same area, shape and relative position, has frequently been used to estimate the capacity between the surfaces\*. The principle has also been used in the investigation of the electro-magnetic field of machines. In the present case it has been employed to enable a measurement of high-frequency resistance of the leads and plates of an air-condenser to be obtained. The condenser is immersed in a suitable electrolyte and the resistance from terminal to terminal is measured. Allowance is then made for the electrolytic resistance, which is usually a small proportion of the total, by determining the specific resistance of the electrolyte and employing the relationship†  $R = K\rho/4\pi C$ , where  $R$  is the electrolyte resistance (in absolute units),  $K$  the constant of the dielectric,  $C$  the capacity of the condenser when used normally, and  $\rho$  the specific resistance of the electrolyte.

### *An alternative method of measurement*

Alternatively, the condenser is immersed in several solutions, having different values of  $\rho$ , and the resistance measured from terminal to terminal is plotted to a base of  $\rho$ . On extrapolating to the axis where  $\rho = 0$ , the intercept gives the required terminal and plate resistance.

### *Errors to which the method is liable*

The method is liable to two important sources of error, but it is possible to avoid them and to obtain a very fair accuracy of result. The first of these is the possibility that at high frequencies the eddy-currents in the electrolyte may modify the lines of current-flow. A theoretical estimate of the limit of this error in any particular case may, however, be made. Let it be assumed that the overall diameter of the condenser is 20 cm. and that the frequency of measurement is  $10^8 \sim$ . The electrolyte may be considered to be a circular conductor of this diameter, and if the calculated high-frequency resistance of such a conductor does not differ appreciably from the D.C. value it is probably safe to assume that the lines of the current-flow between the plates of the condenser when immersed in the electrolyte are an accurate replica of the lines of force between the plates when the condenser is used normally. If this is so the current distribution and consequently the "skin-effect" in the plates and leads will be identical in the two cases. A suitable

\* A. E. Kenelly and S. E. Whiting, *Elec. World*, 48, 1238 (1906).

† *Loc. cit.*

value of  $\rho$  is 50 ohms/cm./cm.<sup>2</sup> Actually electrolytes having values between 20 and 300 ohms have been employed.

The value of  $z$  in the formula  $z = \pi d \sqrt{2f/\rho}$  is 0.4 and from the tables\*  $F$  is 0.000, consequently  $R_{Mf} = R_{dc} \times (1 + F) = R_{dc} \times 1.000$ . Thus it should be perfectly safe to employ an electrolyte of the above resistance in any ordinary condenser at  $f = 10^6 \sim$ .

The second source of error mentioned above is that the boundary surface of the electrolyte in which the plates are immersed may not coincide with that of the dielectric when the condenser is used normally. This error may be reduced to a negligible minimum for all but the lowest settings of a shielded variable air-condenser by suitably shaping the vessel in which the plates are immersed. At the lowest readings, however, the error becomes appreciable.

The readings given in Table 1 illustrate the limits which are imposed by the two errors just discussed:

Table 1

Frequency  $10^6 \sim$ . Variable air-condenser No. 1950.  
Electrolyte: common salt dissolved in tap-water.

Con- denser setting ( $\mu\mu F$ )	Approximate strength of solution											
	$N/2$			$N/5$			$N/10$			$N/20$		
	Value of $\rho$ (ohms)											
	33.5			65.7			111			182		
	Resistance (ohms)											
	$A$	$B$	$C$	$A$	$B$	$C$	$A$	$B$	$C$	$A$	$B$	$C$
1144	0.15	0.0026	0.14	0.13	0.0051	0.12 <sub>5</sub>	0.13	0.0086	0.12	0.13	0.0141	0.11 <sub>5</sub>
889	0.14	0.0033	0.14	0.13	0.0065	0.12 <sub>5</sub>	0.13	0.0111	0.12	0.14	0.0181	0.12
693	0.14	0.0043	0.14	0.14	0.0084	0.13	0.14	0.0142	0.12 <sub>5</sub>	0.14 <sub>5</sub>	0.0232	0.12
443	0.14 <sub>5</sub>	0.0067	0.14	0.15	0.0131	0.14	0.16	0.0222	0.14	0.17	0.0363	0.13
325	0.15	0.0091	0.15	0.16	0.0179	0.15	0.17	0.0303	0.14	0.19	0.0495	0.14
208	0.16	0.0142	0.15	0.18	0.028	0.15	0.21	0.0473	0.16	0.25	0.0773	0.17
92	0.17	0.0322	0.14	0.22	0.063	0.16	0.29	0.107	0.18	0.39	0.174	0.22
57	0.17	0.052	0.12	0.23 <sub>5</sub>	0.102	0.13	0.34	0.172	0.17	0.50	0.281	0.32

Columns *A* give the total measured resistance, employing the resistance substitution method.  
Columns *B* give the resistance of the electrolyte calculated from the measured values of  $\rho$ .  
Columns *C* give the difference between *A* and *B*; i.e. the lead and plate resistance.

So far as the eddy-current error is concerned, it would appear from the results that its effect is just appreciable when the  $N/2$  solution is used, but negligible with the more dilute solutions.

The error due to the impossibility of completely replacing the dielectric with electrolyte is apparent in the increase in columns *C* with decreasing condenser setting, particularly with solution  $N/20$ . The total measured resistance would, of course, be lower in these cases if complete substitution were possible. The discrepancy is greater in the readings just given than in those subsequently obtained, as insufficient care was taken in filling the condenser-casing with the solution.

\* S. Butterworth, "The Effective Resistance of Inductance Coils," *Exp. Wireless*, 3, 207 (1926).

Subsequently it was found that the error was negligible down to a setting of about  $200\mu\mu\text{F}$ .

The important point brought out by these readings is that the electrolyte, although having a specific resistance high enough to ensure freedom from eddy-current error, may yet have an effective resistance, when in the condenser, low enough to enable measurement of the plate and lead resistance to be made with reasonable accuracy.

*An experimental example*

As an example of the usefulness of this method the following experiment may be quoted.

An air-condenser which was being used at very high frequency was suspected of having an unduly high resistance. Upon immersing it in a suitable container filled with electrolyte the following results were obtained:

Frequency $5 \times 10^6 \sim$			
Solution strength	N/3	N/6	N/10
Resistance* (ohms)	2.04	2.11	1.73

Upon repetition the readings were found to be very irregular, ranging from 1.5 to 2.5 ohms. The condenser was therefore taken to pieces and all surfaces between which electrical contact was important were carefully cleaned. When the instrument was being reassembled, all nuts were screwed up tight and heavy gauge copper wires were carefully soldered from plate to plate on both the fixed and moving systems.

The readings were then:

Frequency $5 \times 10^6 \sim$			
Solution strength	N/3	N/6	N/10
Resistance (ohms)	0.27	0.27	0.28

As a final test of the consistency of the results obtainable, the condenser previously used (No. 1950) was taken to pieces, cleaned and rebuilt, and the measuring circuit was arranged to give as great a sensitivity as possible.

The readings then obtained are shown in Tables 2 and 3.

Table 2

Frequency  $10^6 \sim$ .      Condenser No. 1950.

Strength of solution ...	N/2	N/5	N/10	N/20
Value of $\rho$ (ohms) ...	34.2	64.5	108	183
Condenser setting ( $\mu\mu\text{F}$ )	Resistance* (ohms)			
1153	0.154	0.133	0.126	0.121
892	0.141	0.128	0.119	0.113
688	0.136	0.126	0.112	0.114
439	0.129	0.124	0.110	0.111
319	0.126	0.123	0.109	0.104
208	0.122	0.119	0.112	0.110

\* The electrolyte resistance was negligibly small.

Table 3

Frequency  $0.5 \times 10^6 \sim$ .

Condenser No. 1950.

Strength of solution ...	$N/2$	$N/5$	$N/10$	$N/20$
Value of $\rho$ (ohms) ...	34.2	64.5	108	183
Condenser setting ( $\mu\mu F$ )	Resistance* (ohms)			
1153	0.08 <sub>1</sub>	0.07 <sub>4</sub>	0.07 <sub>4</sub>	0.06 <sub>9</sub>
892	0.08 <sub>0</sub>	0.07 <sub>3</sub>	0.07 <sub>1</sub>	0.06 <sub>7</sub>
688	0.07 <sub>9</sub>	0.07 <sub>1</sub>	0.06 <sub>9</sub>	0.06 <sub>5</sub>
439	0.07 <sub>6</sub>	0.06 <sub>8</sub>	0.06 <sub>7</sub>	0.06 <sub>2</sub>
319	0.07 <sub>3</sub>	0.06 <sub>8</sub>	0.06 <sub>8</sub>	0.06 <sub>0</sub>
208	0.07 <sub>4</sub>	0.07 <sub>4</sub>	0.06 <sub>8</sub>	0.06 <sub>6</sub>

\* The electrolyte resistance has been subtracted throughout.

The results in Table 2 are somewhat high for  $N/2$  and  $N/5$  and in Table 3 for  $N/2$  solution when compared with the remaining figures, indicating a tendency for eddy-current effects to modify the value of the resistance as measured. There is throughout a decrease of resistance as the condenser setting is decreased.

The insulation resistance of condenser No. 1950 was measured by the method indicated at the outset, with the result shown in Table 4.

Table 4. Insulation resistance of condenser No. 1950

Frequency ~ Equivalent series resistance at minimum setting of 64.7 $\mu\mu F$ (ohms)	$0.5 \times 10^6$	$10^6$	$2 \times 10^6$	$4 \times 10^6$
	7.985	3.74	1.81	0.91

On the assumption that the parallel resistance equivalent to the insulation losses is independent of the condenser setting, which is probably justified in view of the non-distributed nature of the leakage path, the results in Tables 2 and 4 may be used to obtain the total condenser resistance at various settings.

Table 5

Frequency  $10^6 \sim$ .

Condenser No. 1950.

Condenser setting ( $\mu\mu F$ )	Insulation loss— equivalent series resistance (ohms)	Plate and lead resistance (ohms)	Total resistance (ohms)
64.7	3.74	(0.11)	(3.85)
100	1.56	(0.11)	(1.67)
208	0.36	0.11	0.47
439	0.08	0.11	0.19
688	0.04	0.11	0.15
892	0.02	0.12	0.14
1153	0.01 <sub>2</sub>	0.13	0.14 <sub>2</sub>

At these high frequencies, with the large electrode surface-area of the condenser when immersed in electrolyte, the effect of electrode capacity and its losses may be ignored. It necessitates only a very slight readjustment of the tuning of the test-circuit when the immersed condenser is switched in and out of circuit during the measurement of its resistance by the resistance substitution method.

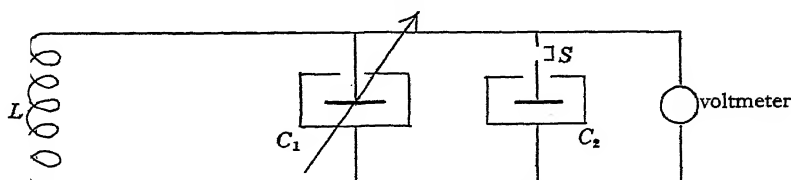


Fig. 1. Resonant circuit employed in measuring the insulation losses in  $C_1$ .

### § 3. ACKNOWLEDGMENTS.

The experimental work has been carried out at the City and Guilds (Eng.) College, where the author has had the advantage of discussing his results with Professor C. L. Fortescue, O.B.E., M.A., and Assistant-Professor E. Mallett, D.Sc.

### DISCUSSION

The author, when introducing the paper, mentioned that the work had been done, for the most part, nearly two years before its publication. This explained why no reference was made to results recently published on the same problem. There are important points, both of agreement and disagreement, between the author's results and those obtained by Mr Willmote\* and Dr Dye†. In the present paper it is shown that the solid insulation losses have an equivalent series resistance very closely proportional to  $1/f$ . In both of the papers quoted the solid insulation is found to have a constant power-factor. On the other hand, Mr Willmote finds that the remaining losses may be represented by a fixed series resistance, whereas the author's results indicate a rapid increase of this term with frequency. If such losses are ascribable to "skin-effect," one would certainly expect an increase with frequency.

Mr ALBERT CAMPBELL (communicated): It is difficult to interpret the expression ohms/cm./cm.<sup>2</sup> used by the author to denote units of resistivity; the use of one solidus following another is confusing. The ordinary, and to my mind the more rational, notation for such units is ohm-cm. or microhm-cm.

Mr G. L. ADDENBROOKE: I do not pretend to have had much experience with the measurement of the losses in condensers at high frequency, though I have done a good deal of work at power and telephone frequencies; nor do I feel

\* "A Quick and Sensitive method of measuring Condenser Losses at Radio-Frequencies," *Journ. Sci. Instruments*, Dec. 1928.

† "Basic measurements of the Effective Resistance of Condensers at Radio Frequencies," *Proc. Phys. Soc.* Vol. 40, Pt 5 (1928).



competent on theoretical grounds to compare any advantages there may be in the author's methods with those of other methods of obtaining the losses in air condensers and their plates. On practical grounds, however, I should have considerable hesitation in applying the method to a condenser on whose after performance I placed any serious value. Not long after the war I purchased several air-condensers with the view of seeing how far they could be used as standards, and made measurements of their dielectric losses and general characteristics. Without going into details, I may say that I found greater differences in the losses than one would have expected from a general inspection of the condensers themselves. I also found that the losses differed from day to day as the moisture in the air varied. In this connection I would point out that surface leakage with alternating currents cannot be predicted from ordinary insulation measurements. In a short paper which I read before the Society in 1912, I showed that even at ordinary frequencies the losses over the surfaces of the class of materials employed in insulating condensers may readily be a hundred times as great, and possibly more at high frequencies. In fact in their general nature they follow the characteristics of the losses through dielectrics; the losses arise, apparently, from the presence of moisture in both cases. To wet the surface of a dielectric and to anticipate that, by drying, you will in a measurable time bring it again to exactly the state in which it was before, is a very doubtful proceeding. I once or twice experienced much trouble and difficulty from moisture unexpectedly getting in between metal surfaces screwed down on to a dielectric; such moisture may be quite invisible, surface moisture being got rid of for the moment, but it will ooze out and affect the insulation in its neighbourhood for a long time. The insulation of high class air-condensers is a subject which requires much care and judgment, as the insulation of many materials deteriorates with time; and my own view is that once a good insulating surface has been obtained, it should be kept in the dark and in well-dried air to maintain it in the same condition.

Mr L. HARTSHORN: The novel application of the similarity of lines of conduction current flow in an electrolyte, and of displacement current flow in a dielectric, has possibilities in considering questions of design, but I do not think it should be regarded as a general method of test for variable air-condensers. Very few insulators, if any, can be immersed in an electrolytic solution without suffering a change, so that the losses in the solid dielectric will probably be quite different after the test from what they were before it.

Prof. F. L. HOPWOOD: I should like to call attention to the fact that the resistances of electrolytes at frequencies of the order of one million do not vary regularly with concentration when high dilutions are being used\*.

The PRESIDENT: I should like to ask whether the author has studied the effect of the large dielectric constant of an electrolyte in altering the distribution of high frequency current in a condenser, and especially the distribution of the displacement current in the insulators wherein the dielectric losses presumably occur.

\* See "Diathermie," by Bordier, Paris 1928, and Fabry, *Comptes Rendus* (1927).

The immersion in an electrolyte would doubtless directly affect the value of the surface resistivity of the submerged parts of the insulation. The method proposed is bold and ingenious, and I hope the author will study it further and justify it against the above and similar criticisms.

Prof. E. MALLETT: As the author mentioned in introducing the paper, when his work was done there was no direct method (apart possibly from a thermal one) of measuring the losses in an air-condenser at high frequencies, and no attempt had been made to separate the losses into those due to the insulation of the condenser and those due to the high frequency resistance of the plates. In these circumstances I think the author is to be congratulated upon his ingenious solution of a very difficult problem.

AUTHOR'S reply: In answer to Mr Campbell: The notation ohms/cm./cm.<sup>2</sup> appears to me to be the briefest way of expressing the resistance of 1 cm. length of a conductor of 1 cm.<sup>2</sup>. cross-sectional area, and is to be preferred to ohm-cm. as being a trifle more definite. Engineers frequently find it convenient to express the specific resistance of copper as  $\frac{1}{58}$  ohm per metre per mm.<sup>2</sup>, and the above notation falls into line with this practice.

Mr Addenbrooke mentions the deleterious effect on solid insulation of immersion in electrolytes. The electrolyte finally selected for my experiments was an aqueous solution of common salt, as this happens to have no appreciable chemical action on either ebonite or the brass and copper portions of a condenser, at least during a brief immersion. It is true that moisture will, under the influence of light, form traces of sulphuric acid from the free sulphur on the surface of ebonite, and that consequently all such insulators should be kept dark and dry, but a measure of exposure is almost unavoidable in practice. In any case solid insulators have to be handled during their construction, and their surfaces must therefore be cleaned subsequently. Thorough rinsing in distilled water and subsequent drying with a clean cloth or leather would appear to be a suitable treatment at this stage, and should prove equally satisfactory after a brief immersion in any electrolyte which has not had a permanent chemical effect on the ebonite.

Mr Hartshorn also mentions that the solid insulation may suffer a change on immersion. I believe I am right in stating, however, that such a stable material as quartz, which is widely used at present in condenser construction, would be quite unaffected by a brief immersion in a solution of salt and that all traces could be subsequently removed by efficient cleansing.

In answer to Prof. Hopwood: The complicated nature of the relationship between the concentration and the specific resistance of electrolytes at high frequency was known to me, and in consequence the actual value of  $\rho$  at each particular concentration, frequency and temperature was experimentally determined.

The President's remarks involve three separate points:

(1) The effect of the displacement current in the solution (as distinct from the conduction current), when the condenser is immersed, in altering the lines of

current flow in the plates and other metal parts. (2) The effect of the displacement current in the solution on the distribution of the displacement current in the solid dielectric and consequently upon the losses therein. (3) The effect of immersion upon the surface leakage on the solid dielectric. With regard to the first of these, the general theorem of the similarity of the lines of current flow between two equipotential surfaces immersed in electrolyte and the lines of the displacement current between similar surfaces in a dielectric appears to be well established (*vide* references on p. 127 of this paper). There are two factors determining exact equivalence in the two cases. These are firstly that the surfaces when immersed shall be equipotential, which is ensured to a high degree of approximation by the relative conductivities of copper and of the electrolyte used; and secondly that the boundaries of the electrolyte shall coincide with those of the electric field. Attention has been paid to these points in the paper. There seems to be no reason why the superposition of a relatively small displacement current in the electrolyte upon the conduction current should involve any alteration in the lines of current flow in it, in view of the fact that both follow similar paths. Consequently it should follow that the eddy-current losses in the metal parts of the condenser should be the same in both cases. So far as the second and third points outlined above are concerned, I have endeavoured in the present method to measure each of the two losses under conditions such that the other is negligibly small. Thus it will be seen from Table 4 that the shunt resistance equivalent to the insulation losses of this particular condenser was nearly 2 megohms at  $f = 10^6 \sim$ . Even if this resistance were reduced very materially by immersion, as would doubtless be the case, owing to alteration of the lines of the displacement current flow in the solid dielectric and to surface leakage, it would still have negligible effect upon the quantity under measurement, which is of the order of 0.1 ohm.

# THE X-RAY STRUCTURE AND MAGNETIC PROPERTIES OF SINGLE CRYSTALS OF HEUSLER ALLOY

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**ABSTRACT.** The X-ray structure of single crystals of Heusler alloy has been examined by the single crystal rotation method. The alloy is found to crystallize as a body-centred cube with lattice constant  $2.95 \text{ \AA.U.}$  The aluminium atoms are distributed so as to lie on a face-centred cube with lattice constant  $= 5.9 \text{ \AA.U.}$  Directional magnetic properties have been studied by a method previously described\* and have been found to be identical with those of nickel which has a face-centred cubic structure. It is suggested that this may be interpreted as indicating that the manganese atoms—whose positions cannot be determined by X-ray analysis—also lie in a face-centred cubic lattice.

## § 1. INTRODUCTION

SINCE the discovery of the Heusler† alloys in 1903, a great deal of work has been done upon them, particularly as regards the effect of heat treatment and ageing. Many of the researches have served mainly to emphasize the complicated nature of the problem, and very little direct evidence has been obtained concerning either the origin of the magnetizability of the alloys or the nature of the changes which take place on ageing‡. X-ray measurements by Young§ and von Harang|| using the powder method have shown that the alloy crystallizes in the cubic system. Young found two types of crystal—a body-centred cube with lattice constant  $3 \text{ \AA.U.}$  and a face-centred cube of  $3.7 \text{ \AA.U.}$  L. von Harang found in addition to these two forms a cubic lattice with a cube side of about  $8.70 \text{ \AA.U.}$

It was thought probable that some valuable information might be obtained if single crystals of the alloys could be grown and examined both as regards crystal structure and magnetic properties. The simplifications introduced both into the magnetic and the X-ray measurements by the use of single crystals give some promise of useful results being obtained along these lines.

\* *Science Abstracts*, no. 1399 (1928).

† Heusler, *Phys. Gesel.* 5, 220 (1903).

‡ See, however, Kussmann and Scharnow, *Zeits. f. Phys.* 47, 770 (1928).

§ Young, *Phil. Mag.* 46, 291 (1923).

|| von Harang, *Zeits. f. Krist.* 65, 261 (1927).

## § 2. PREPARATION OF CRYSTALS

Although the ternary alloys of copper, manganese and aluminium show measurable ferromagnetism over a considerable range of atomic proportions, the strongly magnetizable alloys belong to a fairly small region in which the approximate atomic proportions are two parts copper, one part manganese, and one part aluminium. Similar results are obtained if tin be substituted for aluminium.

Owing to the lower melting points of the tin alloys these were tried in the earlier experiments, but so far they have yielded no single crystals. The aluminium alloys crystallize more readily, the process being as follows: Manganese is added to molten copper in a gas furnace in atomic proportions, one part manganese to two parts copper\*. The binary alloy, which has a melting point of about  $900^{\circ}\text{C.}$ , is then poured into moulds, weighed, and re-melted with the addition of aluminium in the proportion mentioned above. The alloy is well stirred and then poured into a mould, and after the grinding off of any scale the metal is re-melted in a vacuum furnace and cooled very slowly through the melting point. Some difficulty is introduced owing to the rather indefinite melting point and the strong tendency of the alloy to form scale; even when a rapid diffusion pump is used to evacuate the furnace, scale is readily formed (presumably by interaction of the metal with its own adsorbed gas), but two melts have been obtained which contained a number of crystals of useful dimensions. The presence of large crystals was tested by cutting sections, polishing and etching with ferric chloride. In this way single crystals up to roughly  $150\text{ mm.}^3$  in volume were isolated. It is hoped that larger ones will be obtained later on, but it seems hardly likely that crystals of a ternary alloy will be comparable in size with those given by pure metals.

## § 3. X-RAY EXAMINATION

Seven such crystals—five from one melt and two from another—have so far been examined by the single crystal rotation method. The crystals can easily be identified as belonging to the cubic system and were, therefore, mounted with a tetragonal axis parallel to the rotation axis and the ordinary layer line photographs were obtained. The radiation used was the  $K$  radiation of either copper or molybdenum from a Shearer tube. In some ways the copper  $K$  radiation is inconveniently long, but it has several advantages over the molybdenum  $K$  radiation. Firstly, the Shearer tubes are more efficient with copper anticathodes than with molybdenum anticathodes. Secondly, in examining a crystal face of a highly absorbing substance like Heusler alloy, certain planes fail to give reflections owing to the reflected ray being in such a direction that it is unable to escape from the crystal. The shorter the wave-length the greater is the probability that this will occur. Fig. 1 indicates how the molybdenum radiation may fail to escape from a crystal, whereas with copper radiation, which has a bigger glancing angle, the reflected ray can emerge.

\* In practice an excess of manganese is used to allow for oxidation. We are now, however, building an induction furnace and hope by vacuum melting to make more certain of our proportions.

All the crystals so far examined conform with the structure given in Fig. 2. The cube, which has an edge measuring 5.9 Å.U., contains sixteen atoms and can be divided up into eight smaller body-centred cubes having aluminium atoms at

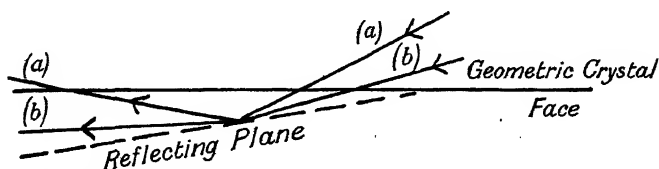


Fig. 1. (a) Copper  $K$  radiation which can emerge after reflection. (b) Molybdenum  $K$  radiation which cannot emerge after reflection.

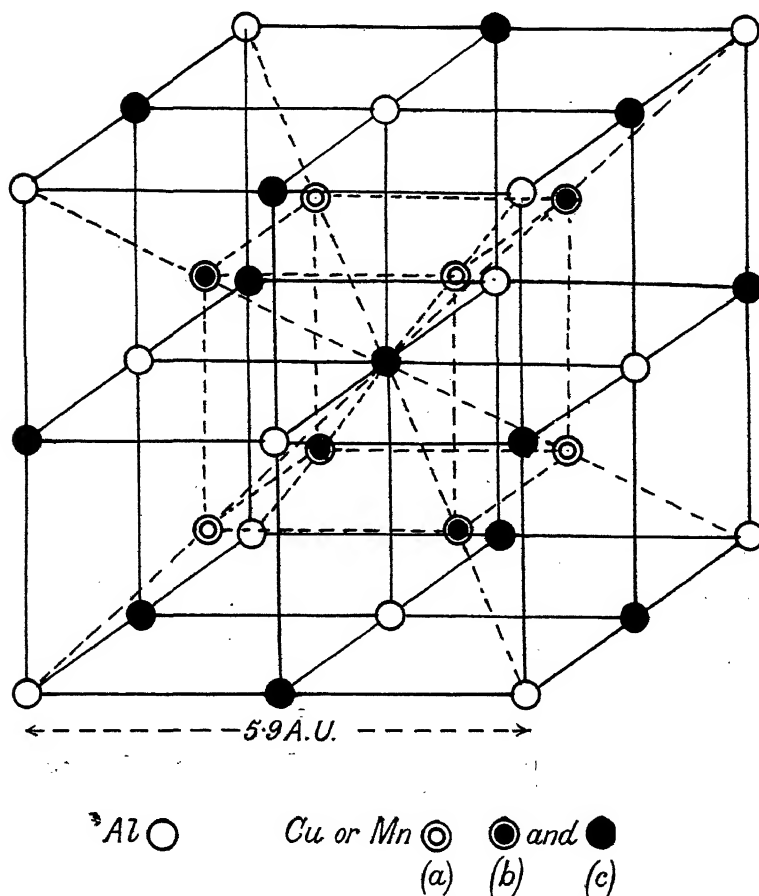


Fig. 2. Crystal structure of the Heusler alloys.

alternate cube corners. This smaller cube is similar to that obtained by Young and by von Harang, but whereas the latter speaks of the lattice as being homogeneous we have obtained definite evidence of the existence of planes of low scattering power which has enabled us to fix the position of the aluminium atoms. It is on

account of this that we have been compelled to choose a unit cell having twice the linear dimensions of that chosen by von Harang. For planes with three odd indices the identity period is four times that for the corresponding homogeneous lattice. If two indices be odd and one even, the identity period is unaffected by the heterogeneity. If two indices be even and one odd, the identity period is twice that of the corresponding homogeneous lattice. The high symmetry of the structure was verified by an X-ray examination of one of the crystals by rotation about each of its three tetragonal axes\*.

It has not been possible to distinguish between the positions of the copper and the manganese atoms by means of X-rays. This would require a very careful investigation of the intensities of different order reflections, which would be made very difficult by the high absorption which takes place in the crystals. Some suggestions as to the possible positions of the manganese atoms will be offered in the discussion of the magnetic results.

In order to obtain single crystals it is not necessary to have exact atomic proportions. Several crystals were analysed, and all contained a slight excess of copper. Presumably the atoms are mutually replaceable in some degree at least.

#### § 4. DIRECTIONAL MAGNETIC PROPERTIES

If a magnetic field be applied along one of the symmetry axes of the crystal the field and intensity coincide in direction, but if the field be applied in any other direction the intensity will not be along the field direction and may be resolved into a component ( $I_P$ ) parallel to the field, and one ( $I_N$ ) normal to the field. The methods of measuring these two components for varying direction of the applied field have been fully discussed in a previous paper†. Unfortunately, the ballistic method formerly used to study the parallel component in nickel was too insensitive for use with the Heusler crystals. This decrease in sensitivity was not wholly due to the Heusler crystals being less magnetizable than the nickel, but mainly to a reduction in size of the crystals, and the consequent increase in the proportion of "uncut" lines. It was necessary, therefore, to use the torsion method for the measurement of both the parallel and normal components of magnetization.

Now in view of a recent criticism‡ of the torsion method for the measurement of the parallel component it would at first sight appear that the use of this method is unsatisfactory. But it may be pointed out that in the case of nickel the results obtained by the two methods differed quantitatively rather than qualitatively. It will be seen below that the use of the torsion method in the present investigation is restricted to a comparison of the results for Heusler alloy with those of nickel. In that case the conclusions are not invalidated, although in its general application the method is unsatisfactory.

\* Since this paper was written, a letter by E. Persson has appeared in *Naturwissenschaften*, 31, 613 (1928) on the X-ray examination of polycrystalline material. He reaches conclusions similar to ours.

† Sucksmith, Potter and Broadway, *Proc. Roy. Soc.* 117, 471 (1928).

‡ *Ibid.* p. 482.

Three specimens prepared in disc form with the plane of the disc in one of the principal crystal planes have been examined. After the planes had been accurately located by X-ray measurements the discs were prepared by the method previously

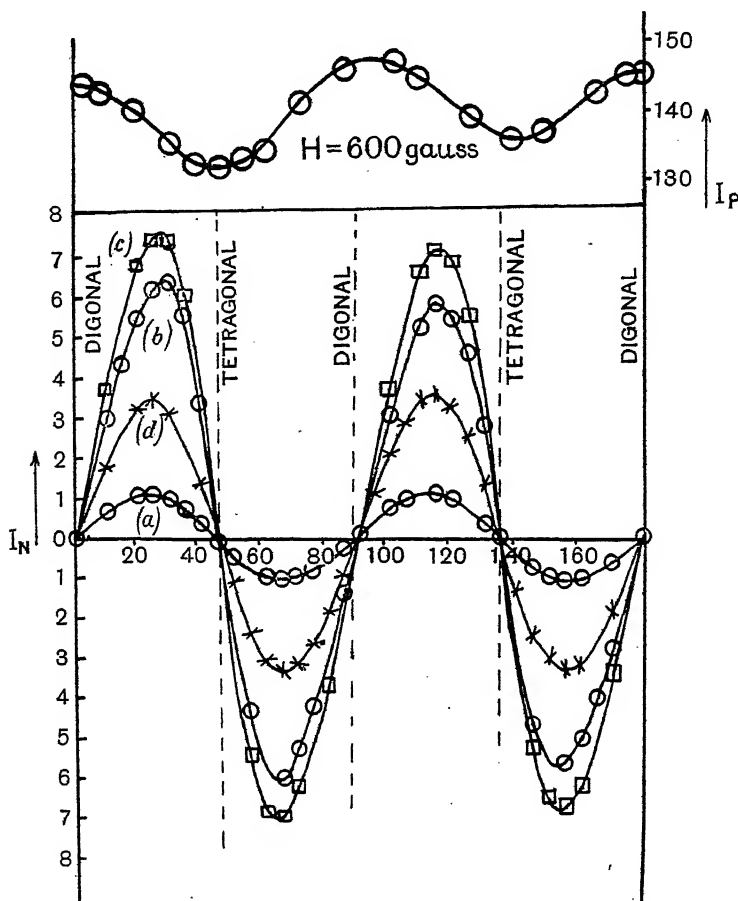


Fig. 3. Relation between magnetization and direction of field (abscissa) in  $\{100\}$  plane.

$I_P, I_N$ , magnetization parallel and normal to field.

$H = (a) 6500$  gauss.  $(b) 2180$  gauss.  $(c) 1110$  gauss.  $(d) 515$  gauss.

described\*. The diameters of the specimens used were the largest which could be produced. The results obtained in the three principal planes were as follows:

$\{100\}$ Plane	Diameter of specimen = 0.280 cm.
	Thickness = 0.028 cm.
	Weight = 0.0112 gm.

The results in this plane are shown in Fig. 3. They are qualitatively identical with those obtained with nickel\*, the maximum magnetizability being along the digonal

\* Sucksmith, Potter and Broadway, *loc. cit.* p. 472.



axis, and the quasi-unstable position of the normal component along the tetragonal axis.

$\{110\}$ Plane	Diameter of specimen = 0.278 cm.
	Thickness = 0.025 cm.
	Weight = 0.0098 gm.

The results are shown in Fig. 4. Except for a somewhat more marked difference in size between the large and small loops the curves are again very similar to those

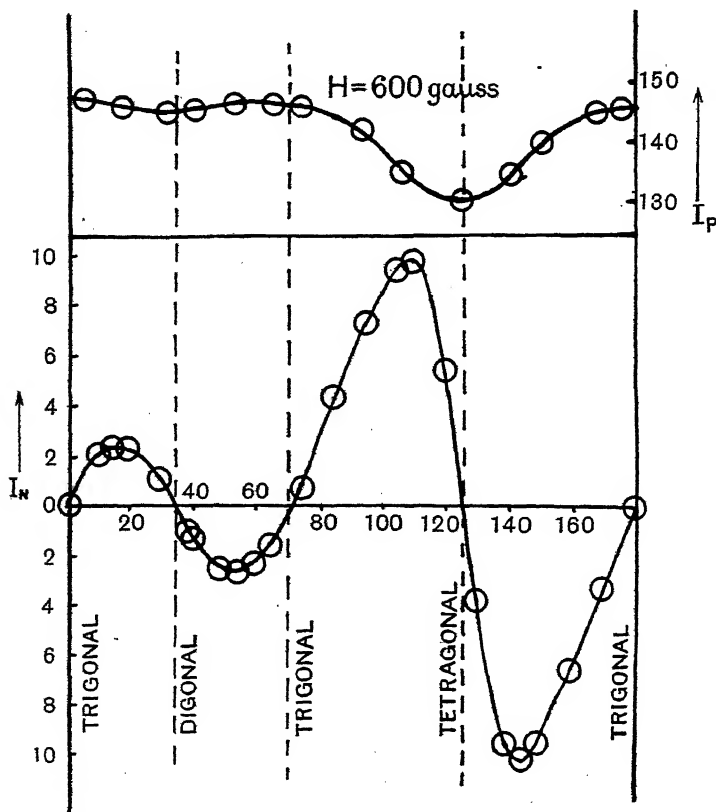


Fig. 4. Relation between magnetization and direction of field (abscissa) in  $\{110\}$  plane.

$H = 600$  gauss for  $I_P$ , 1100 gauss for  $I_N$ .

obtained with nickel. The crystal magnetizes most easily along the trigonal axis and least so along the tetragonal axis. In order to be certain of the reality of the small dip in the parallel component curve, it was necessary to use an air core coil in place of the electromagnet, the field of which was not reproducible with the necessary accuracy.

$\{111\}$ Plane	Diameter of specimen = 0.350 cm.
	Thickness = 0.038 cm.
	Weight = 0.0240 gm.

The curve for the normal component is shown in Fig. 5. Six complete loops appear in  $180^\circ$ . They are not equal in size, but since the maximum value of  $I_N$  is only about  $1\frac{1}{2}$  per cent. of the total magnetization, slight distortion or inaccuracy in cutting the crystal would account for some irregularity in the curves. A  $60^\circ$  period for the normal component in the  $\{111\}$  plane of nickel has been obtained by Kaya\*.

The fluctuations of the parallel component in the  $\{111\}$  plane were too small to be measured. They amounted to less than  $\frac{1}{2}$  per cent. of the total intensity.

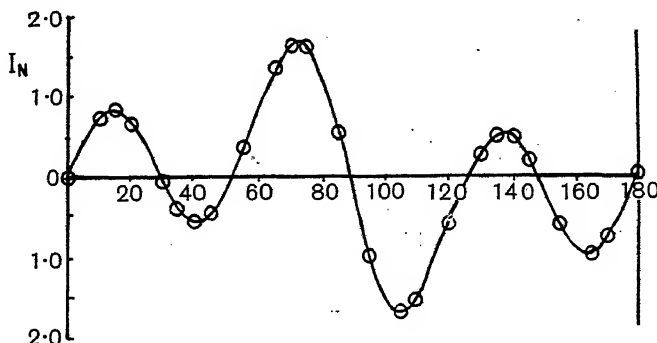


Fig. 5. Relation between magnetization and direction of field (abscissa) in  $\{111\}$  plane.  
 $H=1600$  gauss.

## § 5. DISCUSSION OF RESULTS

The single crystals of Heusler alloy so far examined have all shown a body-centred cubic structure (cube side =  $2.95 \text{ \AA.U.}$ ), the aluminium atoms themselves forming a face-centred cube (cube side =  $5.9 \text{ \AA.U.}$ ).

The directional magnetic properties are almost identical with those of nickel, which belongs to the face-centred cube system, and bear no resemblance to the directional properties of iron† which like Heusler alloy has a body-centred cubic structure. This might be explained if the magnetization is influenced mainly by the distribution of the aluminium atoms. It appears more probable, however, that the important factor is the presence of the manganese, which itself has been obtained in a ferromagnetic condition‡§ and forms several ferromagnetic compounds. On this assumption the directional magnetic properties would probably depend on the spatial distribution of the manganese, present possibly in some modified form which gives it ferromagnetic properties. It seems probable, therefore, that the manganese like the aluminium is arranged in a face-centred cubic structure. This can occur in more than one way while the general structure shown in Fig. 2 is still preserved. Firstly, the circles indicated by (a) and (b), Fig. 2, may be taken to represent copper atoms, and the circles indicated by (c) manganese atoms. The

\* *Sci. Rep. Tōhoku*, 17, 639 (1928).

† Honda and Kaya, *Sci. Rep. Tōhoku*, 15, 721 (1926).

‡ Seckelson, *Wied. Ann.* 67, 37 (1889).

§ Wiess and Onnes, *Compt. Rend.* 150, 689 (1910).

copper atoms would then form a simple cubic system. This arrangement satisfies density considerations, chemical proportions, and X-ray data. If this structure be correct the elementary cubes (of which there are eight in the figure) would have copper atoms at the centres and aluminium and manganese atoms at alternate cube corners. There is, however, at least one other method in which the manganese atoms may be placed in a face-centred cubic lattice without disturbing the general atomic arrangement. The atoms indicated by (*b*) and (*c*) in Fig. 2 may all be copper and the atoms marked (*a*) may be manganese. We should then have four interlocking face-centred cubes, two of copper and one each of manganese and aluminium. It is unfortunate that X-ray intensity measurements cannot so far be made accurately enough to distinguish between these two structures. The work is being continued, and amongst other things it is hoped that it will be possible to study the effects of heat treatment and variation of atomic proportions.

#### § 6. ACKNOWLEDGMENTS

This work has been carried out in the Henry Herbert Wills Physical Laboratory of the University of Bristol. I wish to thank my colleague, Mr S. H. Piper, for the loan of X-ray equipment and valuable help in the X-ray measurements. My thanks are also due to the Colston Research Society of the University for a grant towards the expenses of this investigation.

# A FUSED QUARTZ PENDULUM ROD FOR CLOCKS

By C. V. BOYS, F.R.S.

*Received November 27, 1928. Read and discussed January 25, 1929*

**ABSTRACT.** The author discusses the possible causes of the progressively increasing losing-rate found in the going of the Shortt clock. He shows a design for the free pendulum suitable for use where the rod is made of fused quartz. He would prefer tempered carbon steel for the supporting springs.

IT may be within the recollection of some members of the Physical Society that in the year 1917 Mr C. O. Bartrum read a paper\* before the Society in which he described a free pendulum with slave clock which he had devised and constructed. In this he made an important advance in obtaining a pendulum maintained in motion by uniform gravity impulses delivered once a minute, and having no work whatever to do beyond that inherently necessary in overcoming the imperfection of elasticity in the supporting spring and the viscosity of residual air in an enclosed case. A most important feature of his design was the release of the impulse weight after its operation on the free pendulum to direct the slave clock to hurry or to lag to an infinitesimal extent so as to keep it strictly in phase. The slave clock of course released the impulse device. In other respects the design was unnecessarily complex, but it worked.

In more recent years all previous clock performance has been completely eclipsed by the clocks designed by Mr Shortt and made by the Synchronome Company, and now invading all the observatories in the world. The design of this clock is notable for its extreme simplicity and excellence. Its going is so perfect that its day by day indications are more uniform than day by day intervals determined by star transits. The Astronomer-Royal for Scotland has made a very extensive study of the behaviour of this clock, and two are in operation in our own Royal Observatory. From these observations it would appear that these clocks show a very small but progressively increasing losing-rate, and there is some doubt as to its cause. On the whole the invar pendulum rods are most under suspicion, under the belief that they have the property of growing in length to a very small but real extent in service. Suspicion is also cast upon the elinvar suspension spring.

I have some doubt myself whether the nickel steel alloys are either of them the cause of the trouble. Mr Hope Jones informs me that the bobs of these pendulums have been made of type metal†, undoubtedly good in an ordinary way. Pure lead

\* *Proc. Phys. Soc.* 29, 120 (1917).

† Type metal is probably the best material for the bob, but non-magnetic steel might be worth consideration for this purpose. C. V. B., January 11, 1929.

I should of course condemn, and I have advised a friend to replace a lead bob in a precision clock by one made of gun metal but not of any lead alloy, for the sake of greater stability. As the density of the bob is not of much importance, the pendulum being enclosed in a nearly exhausted case, I should prefer to cut the bob from a bar of rolled mild steel annealed after roughing to form and then finished. The very heavy alloy of tungsten and iron—which is easily made by the thermit process, has a density in the neighbourhood of sixteen, and works beautifully in the lathe—would be worth considering if the pendulum swung in air at full pressure, but the cost and uncertainty attaching to any unproved alloy rule it out for the present purpose. The type metal may or may not be right, but it is a simple thing to try steel. Unfortunately experiments of this kind require some years for completion.

Taking the three elements—rod, spring, and bob—mentioned above, my own view is that in respect of the probability of defect they must be arranged in the following order:

1. *Spring*. Under considerable tension and constantly being bent, but very short.
2. *Rod*. Under far less tension relative to its cross-section and never being bent, but long.
3. *Bob*. Under infinitesimal stress by comparison and short, but of poor material.

At a meeting of the Astronomical Society last winter\* I expressed the view that I should have more faith in a carbon steel rod than in one of invar, but that fused quartz would be the best possible material. It is now forty years since I showed that fused quartz is the one material which possesses all the physical virtues and is devoid of vice, and I believe that subsequent experience has confirmed this view. I find now that in more than one quarter the introduction of a fused quartz pendulum rod is being considered and that one design that has been contemplated is in my opinion hopeless. It seems to me therefore that it is desirable to publish the scheme which I had in mind at the beginning of 1928. The design must be adapted to the properties of the material, with which I am peculiarly well conversant, and need in no way follow that which is suitable for a metal rod.

In Figs. 1-4 I have shown the attachment at the top end, and in Figs. 5 and 6 the attachment to the bob. Fig. 1 is a vertical section through the supporting springs *S*, *S*. Fig. 2 is a plan with the amplitude mirror *M* removed. Fig. 3 is a side elevation. Fig. 4 is a plan of the clamping piece *C* alone. The rod *R* is formed with a boss at each end, and these are ground in a proper grinding lathe so that the cylindrical neck, head and cone are true to a single axis. The clamping piece *C* is saw cut as shown in Fig. 4 to enable it to be put on to the rod and to be pinched on to it. The two inclined saw cuts should be made before the piece is finally cut to form and the free piece should be sweated in place. Then after it is accurately finished in the lathe the piece may be removed by gentle heat and the films of

\* *The Observatory*, 51, 83 (1928).

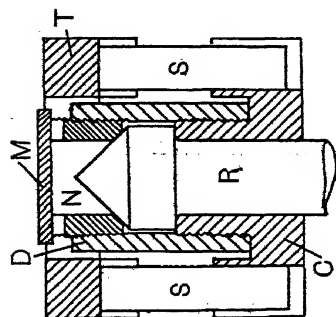


Fig. 1. Elevation, mainly in section, of top of pendulum.

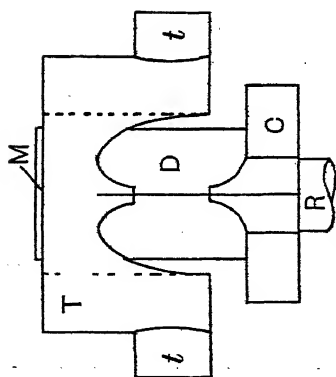


Fig. 3. Side elevation of top.

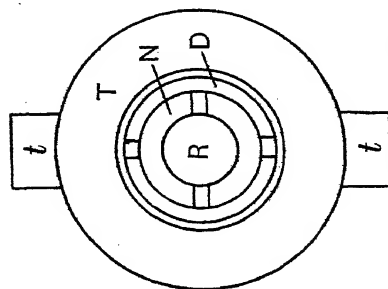


Fig. 2. Plan of top, with mirror *M* removed.

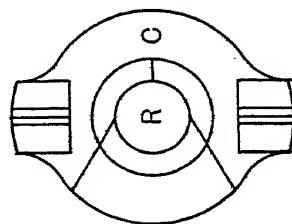


Fig. 4. Plan of clamping piece *C*.

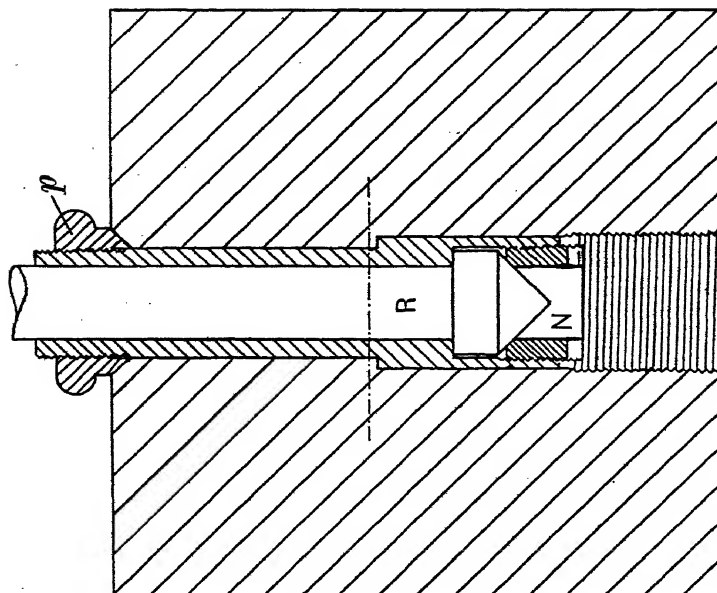


Fig. 5. Elevation mainly in section, of the bob.

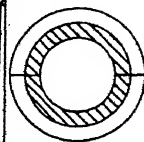


Fig. 6. Horizontal section at dotted line.

solder smoothed down. In this way gaping saw cuts are avoided\*. The two parts of the clamping piece are held together by a tube  $D$  gradually screwed down while it is being ground with fine carborundum up and down the rod and on to its seat. When ultimately the tube  $D$  is screwed down securely the sloping faces of the screw thread will cause the clamping piece to grip the rod, and the nipple  $N$  screwed in firmly will make it certain that the shoulder under the head is firmly upon its seat. The springs  $S, S$  which carry the pendulum are a tight fit in the saw cuts in the clamping piece and in the trunnion gimbal  $T$  which, carried by the actual trunnions  $t, t$ , ensure that the two supporting springs are equally loaded. The supporting springs are sweated in place with solder rich in tin exactly as I described in my article on the grandfather clock†, and the observations I there made on this mode of attachment are, I hope, sufficient to overcome the prejudice against soft solder properly used, which is simply due to ignorance. I should prefer tempered carbon steel to any alloy for these springs, and non-magnetic steel for the whole of the parts at the top end. It will be seen then that the trunnion axis, the plane of attachment to the rod and the centre of the springs are all at one level and that differential expansion is eliminated.

Figs. 5 and 6 show the attachment of the bob. Here the clamping piece is made in two halves sawn after roughing, sweated, finished to form and separated again and ground to the rod, all as already described for the upper clamping piece. Here again the plane of resting is exactly defined and the rod is fixed centrally by the action of the nipple  $N$  bearing on the cone of the rod and elbowing the halves of the clamping piece against the inner wall of the bob. A pinching nut  $p$  both causes the clamping piece to grip the rod at the level of the nut and ensures firm contact between the supporting shoulder of the clamping piece and the bob. The rod and bob are thus relatively defined in position. I have shown this shoulder a certain distance  $x$  above the quartz shoulder and the quartz shoulder a certain distance  $y$  below the centre of oscillation of the bob. These two distances  $x$  and  $y$  can only be determined when the material and size of the bob are decided upon. It will be seen that the distance  $x$  is available for the purpose of any compensation which may be necessary, and the material of the clamping piece will be determined accordingly. The screwed hole at the lower end of the bob is available to take a timing plug or to hold any device which it may be desired to attach at the lower end of the pendulum.

While of course there is no absolute proof that a fused quartz pendulum rod will not gradually lengthen in service, the extremely perfect behaviour of this material and its very simple constitution and high melting-point all lead to the conviction, amounting practically to a certainty, that it will not.

\* The clamping pieces should be of non-magnetic steel. The saw cuts for the springs should be not less than  $1/16$ th in. thick, so that they may be milled with accuracy with a proper milling tool in a machine. The spring must be made up to the required thickness at each end by folding a strip of tinned brass (or even iron) over it so as to ensure a good fit. This arrangement will also facilitate sweating, which must be done in a jig. C. V. B., January 11, 1929.

† *Journ. Sci. Instr.* 3, 143 (1925).

## DISCUSSION

Mr A. CAMPBELL (communicated): I think that Prof. Nagaoka told me in 1924 that he had constructed a pendulum of fused quartz. In his paper on pendula\* he advocates the use of tungsten as a specially suitable material.

Dr D. OWEN: I recall the meeting of this Society at which one of our Fellows, Mr Bartrum, read his paper (to which Prof. Boys so eulogistically referred in the present paper) on the subject of a precision clock consisting of a free pendulum and a slave pendulum. That paper was perhaps the first scientific publication embodying that fruitful idea. Prof. Boys, then our President, was in the Chair on that occasion, and took part in the discussion that followed, as did also another great experimental physicist, the late Mr Duddell. It appears from the present paper that Prof. Boys, in order to secure mechanically good material, has no compunctions about employing mild carbon steel for the bob and for the mountings at the top and bottom of the quartz rod of his free pendulum, although the coefficient of expansion of this steel is large and it is highly magnetic. In regard to the expansion effect, presumably the differential action allows of virtually perfect compensation. But it appears as if the magnetic effect might introduce a control couple amounting to several parts in a million of that due to gravity, so that the effect of secular change in the vertical component of the earth's magnetic field might in time be not inappreciable. Doubtless this field might be compensated, should this be really necessary.

Dr J. H. VINCENT: I think that experiment alone will be competent to decide whether fused quartz extends under long continued tension. The remarkable physical properties of this material seem at variance with the view which regards it as merely an exceedingly viscous solid. It may turn out that even fused quartz will flow under tension to an extent which the very sensitive test of the pendulum will render evident. But even so it might make a better pendulum than invar: this, being an electrical conductor, will introduce a quasi-viscous effect when swinging in a magnetic field; and it is also magnetostrictive so that its length is a function of the magnetic field. In a free pendulum I suppose the greater the freedom the better. If this is so, it becomes a matter of moment to determine the actual paths of escape of the small periodical doses of energy. It looks as if not only will the free pendulum have to be designed so as to lessen these losses by such means as having double pendula swinging in opposition on a common support, but small effects hitherto tolerated must be eliminated. The pendulum though not conducting should be coated with a very thin layer of a conductor which should be of the same material as the inside of the case, thus keeping the case and its contents at the same electrical potential. The air in the case should not only be at uniform temperature and pressure, but of constant humidity. Finally the case and its contents should be made a region of zero magnetic field.

\* *Phys. Math. Soc. Japan*, 1, 347 (1919).



Mr C. O. BARTRUM: I am unable to express any opinions on matters where the properties of materials are involved. With reference to the steadily increasing losing rate of the Shortt clocks at Greenwich, I may say that Dr J. Jackson, Chief Assistant, who is devoting special attention to these clocks, is coming to the opinion that the change is too great to be attributed only to the lengthening of the invar rods. From the text of the paper it seems that Prof. Boys also has doubt on this point. Dr Jackson is looking for some creeping of the bob and for a gradual movement upwards of the instantaneous axis of bend of the suspension spring.

To those who read astronomers' reports of the rating of clocks it may be pointed out that astronomers make strange use at times of algebraic signs. As when a star decreases in brightness its magnitude increases, so when a clock goes more slowly its rate is said to increase.

Dr Owen's comment on the proposed use of steel with its high coefficient of expansion with temperature in the head of the quartz pendulum is answered I think by the design, in which the steel is so disposed that its expansion cancels out.

Dr Vincent referred to various possible causes of dissipation of energy of the pendulum. Mr Shortt made experiments to determine the effect of reduced air pressure, and he found that the curve of dissipation plotted against density converged towards a point that was not zero with complete evacuation. This residual he attributed to molecular dissipation in the suspension spring.

Mr R. APPELYARD: Apparatus constructed by Prof. Vernon Boys is always characterized by precision beyond the range of prudent criticism. In this pendulum, as in all his work, the precision is not the result merely of extended arithmetic applied to correction factors—it is the reward for extreme care in the choice of materials, in the design of parts, in the selection and use of tools and processes, and in the fitting and manipulation of the whole product of his transcending genius. A few weeks ago I came by chance upon some unpublished notes that passed between Francis Ronalds, of Kew Observatory, and Airy, the Astronomer-Royal, that bear upon the history of the growth of such correcting devices. On January 26, 1847, Airy wrote from Greenwich: "I shall be curious to see your barometer-self-corrected-for-temperature arrangement. There is commonly a fear of failure in self-acting corrections of this character, but I do not know that it is well founded." And again, on February 12, 1847, after mentioning the complication of the machinery of Ronalds' apparatus and the fear that it might go wrong, he added: "The gridiron pendulum is not often to be trusted although it generally acts tolerably well." Airy also warned Ronalds that the law of expansion of metals is not accurately known and is not truly linear. He suggested that a record of the temperature should be kept. The truth is, he realized that even metals and their joints are only human.

Prof. F. L. HOPWOOD: Under the action of intense ultra-violet light fused quartz slowly becomes crystalline with consequent changes in dimensions. Whether the amount of ultra-violet light falling on a pendulum of fused quartz would be sufficient to produce a sufficient change in length to affect its rate appreciably, I do

not know. I would like to ask Prof. Boys where one could obtain the steel of specific gravity 16 which he mentions in his paper.

Mr F. A. GOULD: It occurs to me that the use of fused quartz as the material of the pendulum rod of a high-precision clock may be limited by the presence of electrostatic charges on the rod. Crystal quartz is easily electrified and is very difficult to discharge completely even when X-rays are used for this purpose. I do not know whether fused quartz behaves similarly in this respect, but I should be interested to know whether Prof. Boys has encountered any difficulties of this nature during his long experience with the material. It ought not to be impossible to overcome the difficulty in the event of its interfering with the accuracy of the fused quartz pendulum rod.

Prof. D. ROBERTSON: Prof. Boys' paper has been well timed, for the information recently published anent the going of the Shortt clocks at Greenwich and Edinburgh has probably set others besides myself making enquiries as to why quartz was superseded by invar as the standard material for pendulum rods. I would like to suggest that the plane at which the rod is supported should be higher than the centre of the spring, so that part of the temperature compensation may be given at the top. In a forthcoming article (probably in April) in a series now running in the *Horological Journal*, I have analysed the temperature errors of a particular pendulum and estimated their location as follows:

At the top	- 190 ms/d per 1° C.	(A positive error means that
Distributed	- 46 „	the clock goes fast with
At the bottom	+ 46 „	rise of temperature)

These figures apply to running in a sealed case; if the case be open to variations of barometric pressure, the bottom error becomes + 87.

To reduce the effects of stratification to a minimum, I advocate that the compensator at the bottom should correct only for the bottom error and half the distributed one; the remainder should be dealt with by a second compensator at the top. This is quite easily provided in the design given by Prof. Boys when modified as suggested above.

AUTHOR'S reply: I have to thank Dr Owen for kindly reading my paper in my enforced absence.

Of course it is imperative that all massive material in the pendulum should be non-magnetic, but the tempered carbon steel supporting springs seem to me to be essential.

The point raised by Dr Vincent as to the energy lost by eddy-currents due to the rotation of the bob in the earth's magnetic field is a real one. Whether or not the loss is comparable to the energy which has to be provided, my imagination cannot answer. The loss might be calculated, or as it is proportional to the square of the strength of the field a test could be made very easily by fixing a pair of long thin magnets in the line of the dip, one on each side of the clock so that the field in which the bob moves is reduced to a small fraction of the earth's field. Then in

the course of a few days an increase in amplitude would demonstrate the existence of this loss and its amount. I do not like the double pendulum suggestion. The fused silica rod has one physical virtue which in the present case is a nuisance. It is a perfect insulator\* of electricity or nearly so and to prevent electrification due to any unknown cause it might be necessary to silver it.

In answer to Prof. Hopwood: The piece of tungsten-iron alloy rich in tungsten was given me by General Holden, F.R.S., and I turned it and "played with it." As I said, it is easily made by the thermit method, but I must warn anyone playing with thermit mixtures that there are dangers, as I have seen.

I should be only too glad if Prof. Robertson would go into the detail design and by all means counteract stratification by distributing compensation. There should as a fact be no stratification because no one using a Shortt clock is treating it fairly if he does not have it in a constant-temperature room in which strong air circulation is maintained all the time.

May I in conclusion say that the centre of gravity of this paper is the mode of attachment to the rod of the solid metal parts without shake, without strain and about defined planes; and a minor point is the defiance of the belief prevalent in the horological world that a double suspension spring is undesirable.

\* *Proc. Phys. Soc.* 10, 128 (1889).

# A SURVEY OF HEAT CONDUCTION PROBLEMS

BY EZER GRIFFITHS, D.Sc., F.R.S.

*Lecture delivered on December 14, 1928*

**ABSTRACT.** Several forms of thermal conductivity apparatus are described which have been devised for the study of diverse materials ranging from a sheet of mica to a wall section weighing half a ton. The materials are broadly classified into four groups:

- (1) Materials of very low thermal conductivity, such as cold storage insulators.
- (2) Materials supplied in the form of thin sheets and those employed in building construction.
- (3) Refractories and materials employed in furnace construction.
- (4) Pure metals and alloys.

Samples of baked slab cork are shown with a conductivity as low as 0.00007 c.g.s. unit\*. The insulating value of such materials is due to the fact that they subdivide the air space into a large number of minute air cells. The theory of heat conduction through granular material is an interesting problem. An attempt to work it out mathematically has been made by M. Smoluchowski†. The wide divergence between the results obtained by experiment and those calculated from theoretical considerations indicate that the mechanism of the heat transfer from solid to gas is one which requires further study.

In the testing of materials of low thermal conductivity by the hot plate method attention has to be given to heat leakage from edges and corners. The simplest procedure is to eliminate the effect by the use of a guard plate, but it is also possible to calculate an approximate correction for the "edge effect" when using the simple hot plate method. A mathematical problem awaiting solution with numerous practical applications is the adaptation of the method of conformal representation to three-dimensional problems. Sixty years have now elapsed since the publication of the important papers by Schwarz and Christoffel, and in this interval numerous papers have appeared demonstrating what a powerful tool conformal representation is for the solution of two-dimensional problems. Substances in the form of thin discs can be tested by the divided bar method, the correction for the thermal resistivity of the two mercury films being obtained by independent experiments using a thin disc of iron instead of the specimen. This apparatus is not well adapted for the study of poor heat-conductors, owing to the fact that the temperature drop across the specimen is then large and the gradient along the two bars small. The electrically heated plate, sandwiched between two discs of the material with water-cooled plates on either side, is an apparatus which can be adapted to various substances obtainable in sheet form. A form of this apparatus devised for the study of the effect of pressure on the flow of heat through a pile of paper-covered iron stampings is illustrated. In this test the thermal resistance across the laminations is measured. For the determination of the heat flow along the laminated material a bar about 15 in. long of square section, 2 in. by 2 in., is built up. One end is electrically heated, while the other dips into a pot of mercury carrying a cooling coil. From the temperature gradient and the heat flow the conductivity can be calculated.

The apparatus for the study of refractories consists of a furnace made up of "silit" rod heaters which can raise one face of the slab under test to any temperature up to 1000° C. On the top of the slab is a water-flow calorimeter fitted with a guard ring.

\* The conductivity of air is about 0.00006.

† *Bull. Intern. Acad. Sciences*, Cracovie, 5 A, 129 (1910) and 8 A, 548 (1911).

The calorimeter and guard ring are made of thick slab brass with grooves milled in the back surfaces for water circulation. To reduce heat transfer between calorimeter and guard ring the edges of the plates are chamfered off so that the edges on the brick are near together, whilst the rear parts are well separated. For the study of metals and alloys the guard tube method for the elimination of heat loss sideways is to be recommended in preference to Forbes' procedure. The space between guard tube and specimen is packed with a powder of low thermal conductivity. Both specimen and guard tube can be attached to a cylindrical block containing a heating coil. The heat flow is determined with a cooling coil fixed to the other end of the specimen. Water flows round the end of the specimen and the guard ring so that the same gradient is maintained automatically in specimen and guard tube. In some experiments the guard tube is dispensed with and the heat leakage through the lagging material calculated approximately.

In the study of two groups of alloys—aluminium alloys and bronzes—it has been found that the two groups give values of the Lorentz coefficient approximating to the values for the pure metals which form the principal constituents of the alloys—namely, 5.5 for the aluminium alloys and 5.9 for the copper alloys.

## § 1. INTRODUCTION

IN this lecture I do not propose to deal with the purely theoretical problems in heat conduction which are to be found in abundance in Carlslaw's *Heat Conduction*, Byerly's *Fourier's Series and Spherical Harmonics*, and Ingersoll and Zobel's *Mathematical Theory of Heat Conduction*, but rather with the practical difficulties of the worker who has to determine the thermal conductivity of a material in whatsoever form it is supplied to him. When you have to tackle materials ranging from a sheet of mica to an earthenware duct you never lack variety or troubles!

I propose to give a short survey of the various forms of apparatus which we have employed for the measurement of thermal conductivity, and of their peculiar defects and advantages.

No particular novelty is claimed for the methods, but possibly the experience gained in the course of the study of the most diverse classes of materials may be helpful to others confronted with similar problems. For the purposes of discussion it is convenient to classify materials into the following four groups:

(a) Materials of very low thermal conductivity, of the order of 0.0001 c.g.s., such as are used for "cold storage" insulation.

(b) Non-metallic substances obtainable in the form of thin sheets of medium thermal conductivity of the order of 0.002 c.g.s. and less.

(c) Refractories and materials used for heat insulation at high temperatures. (Thermal conductivity from 0.0002 to 0.005 c.g.s.)

(d) Metals and alloys. (Thermal conductivity from 0.6 to 0.1 c.g.s.)

I shall deal with each of these groups in turn and indicate the special points needing attention in their study.

## § 2. MATERIALS FOR COLD STORAGE INSULATION

The characteristic of these materials is their low thermal conductivity, a coefficient of thermal conductivity of 0.0001 gm. calories per cm<sup>2</sup>. per sec. for 1 cm. thickness and 1° C. difference between the faces being usual for a high grade material. This would be for a cold face temperature of 0° C. and hot face of 15° C. The conductivity increases with temperature. Baked slab cork is obtainable with a thermal conductivity as low as 0.00007 and, when we remember that still air has a conductivity of 0.00006, it will be realized how efficient these materials are. Their insulating value is due, not so much to the fact that the materials themselves are poor heat-conductors, as to the fact that they subdivide the air space into a large number of minute air cells.

Fig. 1 is a microsection of a material composed of gas cells enclosed by membranes of hard rubber.

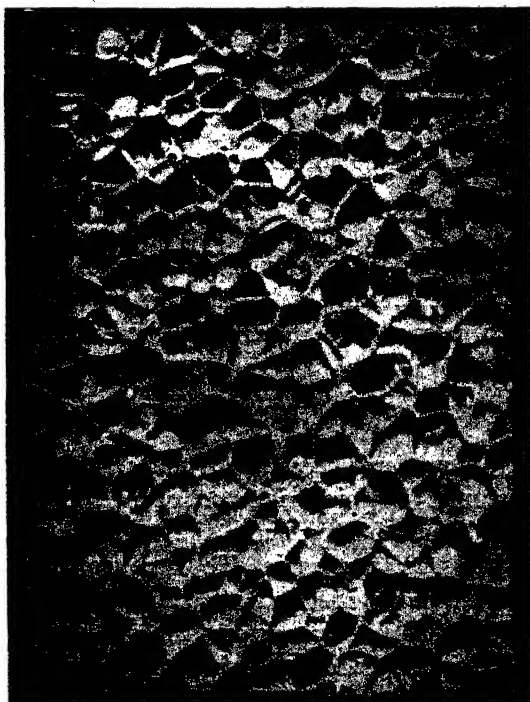


Fig. 1. Microsection of rubber insulating material.

The ideal material for cold storage insulation would be an assemblage of minute gas cells, totally enclosed in a light framework impervious to moisture. The ideal material has not yet been found, but high grade cork granulated, pre-heated, steamed and then run into moulds, and heated under pressure to about 250° C. gives a slab which is a remarkably good insulator, and in practice a material impervious to water is subsequently applied to the surfaces.

*Thermal conductivity data for cold storage insulation*

It may be of interest to quote here a few values selected from the variety of materials which have been studied. In each case the temperature range is from about  $0^{\circ}$  to  $16^{\circ}$  C., although data have also been obtained for various mean temperatures up to  $100^{\circ}$  C. when maintaining the same difference between hot and cold faces throughout the range.

Table 1

Material	Conductivity c.g.s., according to density
Baked slab cork... ..	0.000072 to 0.0014
Granulated cork ... ..	0.00008 to 0.00011
Cork shaving such as is used for cigarette tips	0.000073
Diatomaceous earth ... ..	0.000193
Slag wool, density 15 lb. per cu. ft. ... ..	0.000102
Cellular expanded rubber sheet ... ..	0.00009
Ditto. Clippings packed to 4 lb. per cu. ft. ...	0.000106
Cellular expanded ebonite, 5.4 lb. per cu. ft.	0.000090
Rubber sponge, 14 lb. per cu. ft. ... ..	0.00013
Peat dried and compressed ... ..	0.00009 to 0.00018
Pumice in granulated form ... ..	0.00022

The above list could be extended to many times its length, but it will suffice to illustrate the order of magnitude of the conductivities.

*Theory of heat conduction through granular material*

The theory of heat conduction through powders and granulated substances has been worked out mathematically by M. Smoluchowski\*, who assumes:

- (1) The powder to be made up of perfectly conducting spheres arranged in cubical order.
- (2) That there is a discontinuity of temperature at the interface between solid and gas.

This last assumption is rendered necessary by the fact that there would otherwise be infinite flow of heat near the point of contact of the spheres. Whilst his mathematical work is of fundamental importance, the experiments which he made to verify the formulae were somewhat crude. He used two concentric cylinders, the inner being the bulb of a mercury thermometer whose rate of cooling was observed while the outer cylinder was in ice. The gas pressure was varied from 22 to 760 mm. However, he showed that the conduction through the gas in the interstices of the powder was given by the expression

$$K = \frac{1}{2} \pi k_0 \log_e (1 + a/\delta),$$

where  $k_0$  is the conductivity of the gas,

$a$  is the radius of the sphere,

$\delta$  is the mean free path,  $\lambda$ , of the gas molecule multiplied by a factor determined by experiment.

He found  $\delta$  to be  $1.2\lambda$  for air and carbon dioxide, and  $2\lambda$  for hydrogen.

\* *Bull. Intern. Acad. Sciences*, Cracovie, 5 A, 129 (1910) and 8 A, 548 (1911).

In the second paper Smoluchowski worked out the theory of conduction through a powder in a vacuum. The introduction of spheres of radii  $a$  between the walls  $d$  cm. apart will reduce radiation from  $R$  to  $R \cdot 2a/d$ . If  $d$  be large compared with  $a$  the radiation transfer will be small. He prepared zinc powder by distillation and found it composed of spheres of fairly uniform size 0.028 mm. He then computed the area of contact by Hertz's theory and, assuming perfect thermal contact, found the calculated conductivity to be about 1000 times greater than that found by experiment. He concluded that good thermal contact did not exist between the grains. The mechanism of the heat transfer from solid to gas is one which requires further investigation; it is, for example, conceivable that in the above experiments the zinc spheres were coated with a film of oxide.

Aberdeen and Laby\* studied experimentally the effect of gas pressure on the conductivity of a very light powder, silox, in air, carbon dioxide and hydrogen at pressures varying from 1 to 760 mm. They found the empirical expression

$$k = \frac{1}{2} k_0 \log_{10} (p/n)$$

to represent their results, where

$k_0$  is the thermal conductivity of the gas,

$p$  its pressure, and

$n$  is a constant for the gas.

This expression approximates to Smoluchowski's. It might be noted that these investigators obtained a conductivity value as low as  $0.7 \times 10^{-5}$  c.g.s. for silox in the best vacuum attainable in their apparatus. The use of such a powder in the evacuated space between the walls of metal Dewar vessels would render high polishing of the surfaces unnecessary.

#### *Apparatus for determination of the conductivity of cold storage material*

In tests of coarsely granular material it is necessary to use a test sample whose thickness is large compared with that of the granules. The use of a large sample has the further advantage of giving an average value. The standard form of apparatus employed consists of a hot plate sandwiched between two cold plates. With materials of low thermal conductivity it is essential either to employ a guard ring round the hot plate so as to ensure that the flow takes place along the prescribed paths, or else to make a correction for side loss. It might be remarked here that when a hot plate is inserted between two thick walls of insulating material a calculation based on the assumption that the heat will flow out normally to the hot plate may give results in error by as much as 45 per cent. owing to the leakage of heat from the edges†.

One form of apparatus employed has a 3 ft. by 3 ft. hot plate made of aluminium sheets clamped on to a flat heating coil. The guard ring is 1 ft. wide and separated by a narrow air gap from the hot plate. The two cold plates consist of steel plates

\* *Proc. Roy. Soc.* 113 A, 459 (1926).

† This is true of a plate 3 ft. by 3 ft. surrounded on all sides by an 8 in. uniform thickness of insulating material.



5 ft. by 5 ft. with a grid of pipe screwed on to the back of each. The entire apparatus is slung so that the plates can be moved from the vertical to the horizontal plane. Testing a layer of material both vertically and horizontally will show whether an appreciable amount of convection is taking place in the interspaces. Thermocouples of twin laid copper constantan are used for the measurement of the temperature at various points on the hot and cold faces.

Most of the conductivity measurements on cold storage materials can also be carried out with the apparatus shown in Figs. 2 and 3. The test samples in the form of slabs are 12 in. by 12 in. by about  $1\frac{1}{2}$  in. thick, while powders or granules are enclosed in a frame. The resistor elements of both the hot plate and guard ring are made of nichrome strip threaded through suitably spaced slots in a sheet

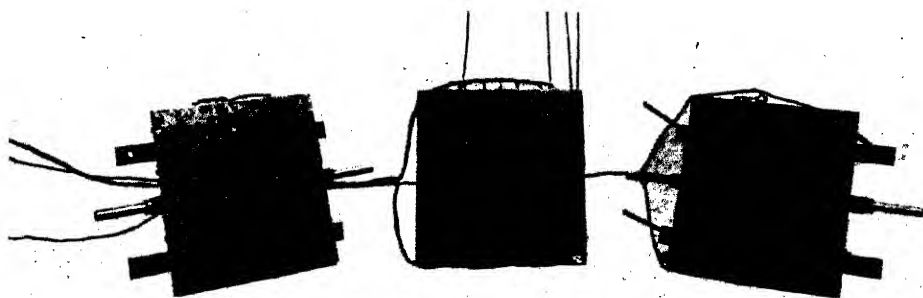


Fig. 2. Electrically heated hot plate with guard ring and two cold plates.

of micanite. Both hot plate element and guard ring are carried on the same sheet of micanite, which is cut away in the region between the hot plate and guard, leaving only narrow connecting tongues so as to ensure maximum thermal resistance. The aluminium plates are clamped on to this micanite sheet, electrical insulation from the winding being effected by exceedingly thin sheets of micanite. A series of copper constantan thermojunctions are attached to the inner surfaces of the metal plates by lead plugs and the wires are carried out in grooves milled in the plates. The cold faces are made up of two surface plates maintained at a constant temperature by water circulation. Surface plates can readily be converted into hollow boxes. Holes are drilled into the plates parallel to the surface and thermocouples are inserted in these.

The arrangement for circulating water or brine at constant temperature through the cold plates needs no explanation. In thermal work the guard ring manipulation is not such a simple matter as in the corresponding electrical problem, for the temperature has to be built up by the dissipation of energy and not merely by

coupling to a fixed potential. The use of a guard ring necessitates some care in adjustment of the temperature of the ring to equality with that of the hot plate. Usually it is possible to make the adjustments so that in one experiment the temperature of the guard ring is slightly higher than the hot plate and in the next that it is slightly lower. If a guard ring be dispensed with it is absolutely essential to allow for the flow sideways when testing thick layers of materials of medium conductivity. The two-dimensional flow is amenable to rigorous calculation by the method of conformal representation, but in practice the flow is in three dimensions, and the three-dimensional flow at a corner cannot be calculated. Another objection to dispensing with the guard ring and using a more complicated formula is the fact that, if uniformity of temperature over the hot plate is to be secured, thick metal plates are necessary; otherwise the increased heat flow at the edges of the hot plate introduces gradients across it.

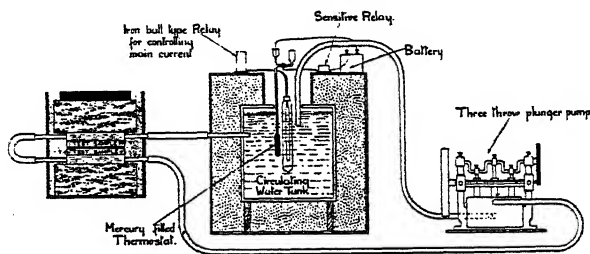


Fig. 3. Arrangement of apparatus for maintaining steady temperatures at the cold faces.

Practical considerations, however, sometimes necessitate the use of a simpler form of apparatus, as, for example, in testing wall sections whose conductivity may be twenty-fold that of cork. In this case the apparatus consists of a hot plate laid on a slab of cork with the test specimen laid on the hot plate. No guard ring is employed with this apparatus, but the heat flow through the cork packing around the edges is allowed for approximately. The hot plate rests on a slab of baked cork about 7 in. in thickness. Disc thermocouples of copper constantan are stuck on to the hot and cold faces of the wall section. The heat flow through the slab of cork covering the back is readily computed, but the calculation of the heat flow sideways is a difficult problem, as assumptions have to be made which can only be roughly correct. For instance, the boundary has to be assumed an isothermal. By making the dimensions of the hot plate large in comparison with the thickness of the material, the edge correction can be made very small—of the order of a few per cent.—in comparison with the flow through the test sample.

#### *“Box” methods of conductivity measurements*

The use of a box containing a heating coil is sometimes advocated for conductivity work, the walls of the box being composed of the material under test. The serious objection to that form of apparatus is that it is not possible to obtain an exact mathematical expression for the heat flow through a geometrical system

of this form. Even for approximate calculations the assumption has to be made that the surfaces are isothermal—a condition which is rarely realized in practice. Probably the simplest method of dealing with a complicated shape is not to attempt a mathematical solution, but to construct an electrical condenser of the same form and determine its capacity with air as dielectric.

### *Two-dimensional heat flow problems*

It is disappointing that no one has hitherto adapted the method of conformal representation to three-dimensional problems. For two-dimensional heat flow problems the theorem of Schwarz and Christoffel\* is a powerful tool for their solution†, but in thermal conductivity measurements we usually have to deal with a three-dimensional problem. Schwarz published his important paper sixty years

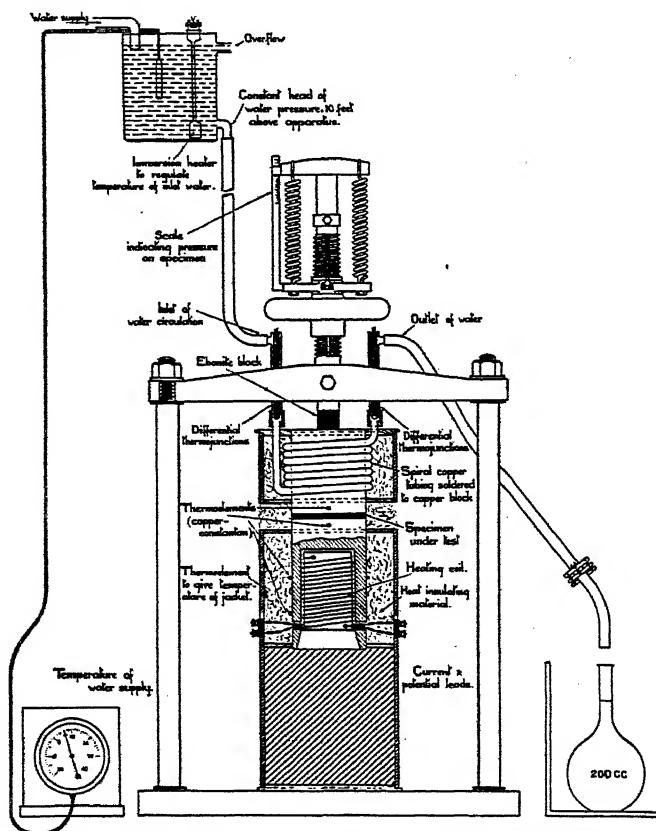


Fig. 4. Apparatus for heat transmission tests on thin discs.

\* "Ueber einige Abbildungsaufgaben," *Crelle*, 70, 105-120 (1869); and "Sul problema della temperature stazionarie," *Annali di Matematica*, 1, 89 (1867).

† The reader who is interested in the theoretical aspect might be referred to an important paper by H. F. Moulton (*Proc. London Math. Soc.* 3, 104) and also to the treatment in J. J. Thomson's *Recent Researches in Electricity and Magnetism*, p. 208, and Jeans' *Electricity and Magnetism*, 4th edition, p. 354.

ago and half a century has elapsed since Kirchhoff\* showed the possibilities of the method in the solution of physical problems. The case worked out by Kirchhoff was that of a plate condenser in an infinite medium.

### § 3. APPARATUS FOR THE DETERMINATION OF THE CONDUCTIVITY OF THIN SHEETS

Data as to the heat transmission through thin sheets of electrically insulating materials are frequently required. Various forms of apparatus have been devised for these tests by Dr Kaye and the writer. In the one shown in Fig. 4 a copper rod  $1\frac{3}{4}$  in. in diameter is hollowed out and a heating coil is inserted, as indicated in the figure. The specimen under test rests on the top surface of this rod and superimposed is a water-cooled rod pressed down by a spring. The top rod is surrounded on its outer surface by a copper spiral through which flows a steady stream of water. The temperature rise of the water is measured by a set of differential thermocouples. The surfaces of the copper bars are ground plane to an accuracy of  $1/10,000$  in.

The essential features of a modification of this apparatus for use with thicker materials are shown in Fig. 5. In this arrangement the heating coil is in the form of a flat disc, and two samples of material are employed in the test.

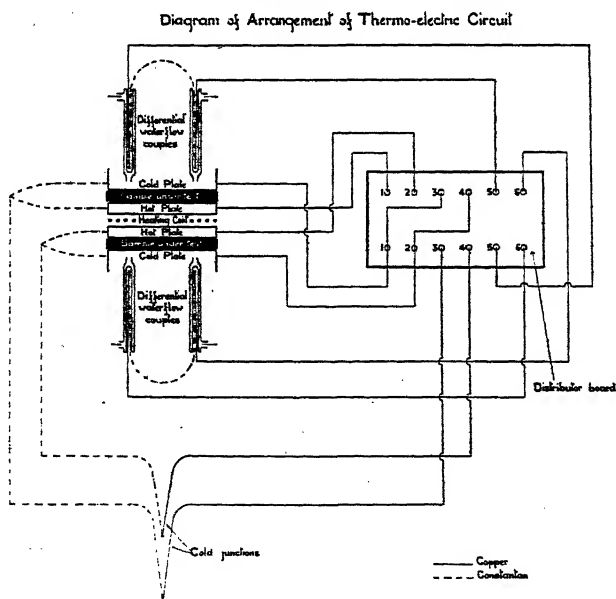


Fig. 5.

The "gradient along a bar" method was also used and found satisfactory for such materials as mica. This apparatus is shown in Fig. 6. One of the bars is provided with a heating coil and the other with a cooling coil, these being attached

\* *Gesamm. Abhandl.* p. 112; *Berlin Akad. Monatsberichte*, p. 144 (1877).

to the extreme ends of the bars. Thermocouples were arranged at regular intervals along both bars so that the temperature gradient could be observed. The bars were supported vertically, the lower one being fixed while the top one was movable. In this apparatus the quantity of heat flowing into the specimen and out of it was obtained by observations of the temperature gradient along the copper bars and a knowledge of the thermal conductivity of the copper.

The two surfaces were amalgamated so that good thermal contact with the specimen was ensured. In order to determine the thermal resistivity of the two mercury films, which were always present when a specimen was interposed between the bars, some tests were made using a sheet of iron 0.002 inch thick instead of the specimen. From observations of the discontinuity in the temperature gradient across the mercury joints and the thermal conductivity of the iron specimen, the resistance of the film was calculated.

It might be mentioned that with this apparatus tests on a sample of mica of two thicknesses, one twice the other, gave very satisfactory agreement between the values of the thermal conductivity. It might also be mentioned that this apparatus is not well adapted for the study of poor heat-conductors

unless thin specimens be used. For if the thermal resistivity of the material be high, the temperature drop across the specimen is large and the gradient along the two bars small. As it is necessary to measure the gradient along the bar, this limits the use of this simple form of apparatus.

To study the variation in the conductivity over the area of a large sheet the apparatus shown in Fig. 7 was designed. The heating coil is clamped between two flat copper plates partially embedded in a block of ebonite: the amalgamated face is horizontal and downwards. The complete heating unit is carried on a spindle working in guides, and once it is properly aligned with the cold plate these guides ensure that the hot face registers correctly with the cold face. This automatic alignment of the two surfaces is essential when point to point tests have to be made on large sheets. The cold surface is the end of a cylindrical block of copper maintained at a constant temperature by the circulation of water. The temperature of the inlet water to the "cold" block is so adjusted that the mean of the inlet and outlet temperatures is equal to the temperature of the surrounding atmosphere: this arrangement eliminates the correction for loss or gain of heat from the block.

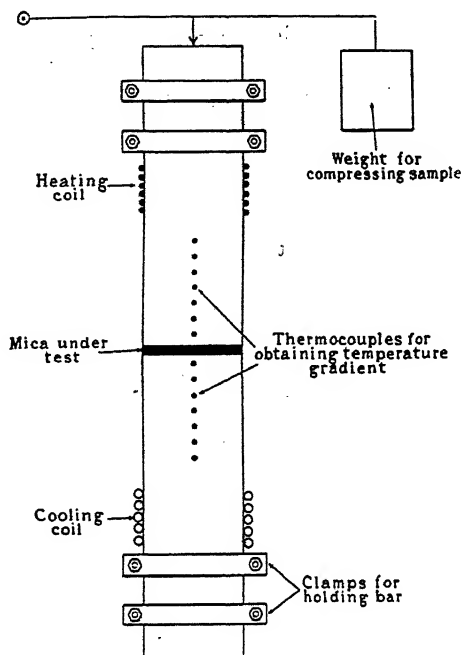


Fig. 6. Apparatus for the "gradient along a bar" method.

The spreading out of the lines of heat flow at the boundary is a point to which attention must be given. The two-dimensional case is amenable to mathematical solution, but not that of circular discs. Probably the simplest procedure if absolute values were desired would be to measure the capacity of a condenser with a sheet of dielectric between the plates.

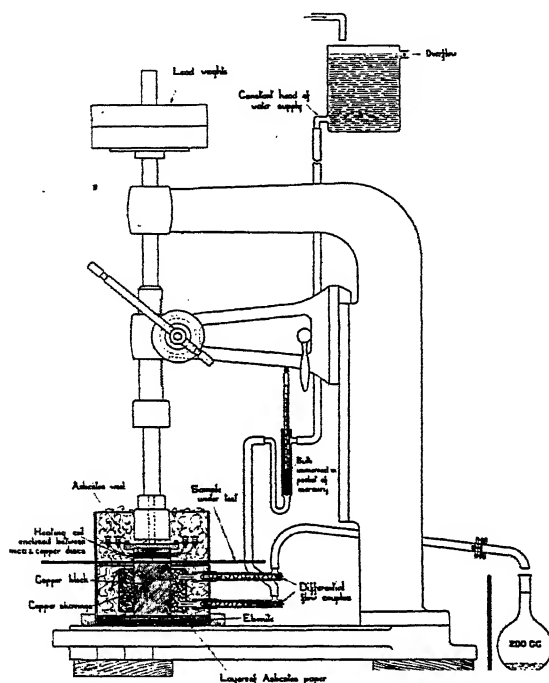


Fig. 7. Apparatus for measuring the thermal conductivity at various points on a sheet of material.

The question of the effect of pressure on the conductivity of material in laminated form is an important one, as, for example, in the case of laminated stampings used in electrical construction. The form of apparatus employed in this connection is shown in Fig. 8 and is self-explanatory. The apparatus is rigidly constructed to withstand the pressure applied by means of three springs. The hot and cold plates are 3 in. in diameter. Now this apparatus, although well adapted for the measurement of the heat transmission across the laminations of the block of stampings, is not suitable for the determination of the conduction along the stampings. For this test a bar about 15 in. long of square section with a 2 in. side was built up and an apparatus of the form shown in Fig. 11 used. One end of the bar was electrically heated, while the other end dipped into a pot of mercury carrying the cooling coil through which a measured flow of water circulated. The temperature distribution of the bar was found by means of thermoelements and the bar was well lagged. A detailed description of this type of apparatus is given later.

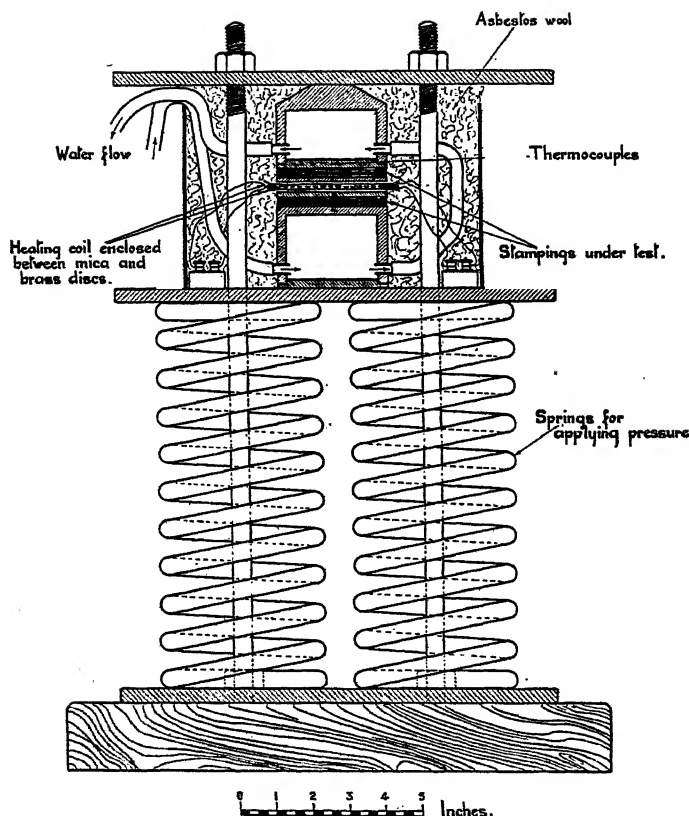


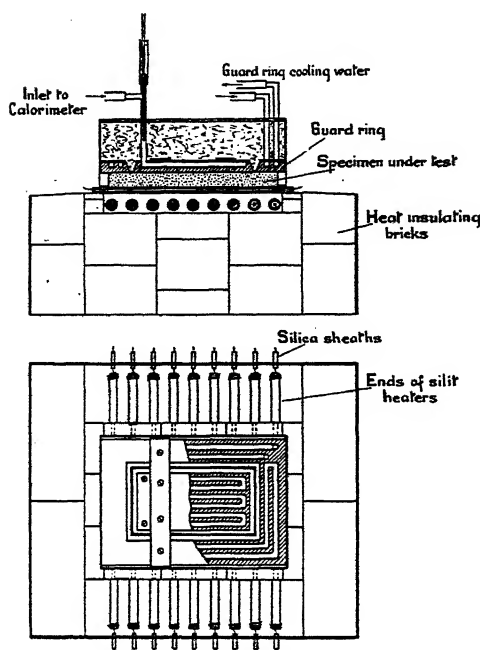
Fig. 8. Apparatus for tests on heat transmission through laminated materials under pressure.

#### § 4. APPARATUS FOR THE DETERMINATION OF CONDUCTIVITY AT HIGH TEMPERATURES

The materials studied at high temperatures have been either refractories of high conductivity or good heat-insulating bricks employed as lining to the refractories. Mention may be made of two forms of apparatus.

In the apparatus shown in Fig. 9 a furnace is built up with "silit" heaters. These heaters are cylindrical rods of a refractory material and can be connected across the mains. A rod  $\frac{3}{8}$  in. in diameter and 10 in. in length will dissipate about 500 watts in free air, the temperature of the surface being then about  $1200^{\circ}\text{C}$ .

The calorimeter and guard ring are made of thick slab brass with grooves milled in the back surface of each for water circulation. To reduce heat transfer between calorimeter and guard ring, the edges of the plates are chamfered off so that the edges on the brick are near together, whilst the rear parts are well separated. The brick rests on a thick flat plate of nichrome, a sheet of micanite being interposed to protect the thermojunction. The water flowing through the calorimeter is supplied from a constant-head tank.



Plan showing ducts for circulation of water  
in Calorimeter and Guard Ring.

Fig. 9. Apparatus for thermal conductivity tests at high temperatures.

#### § 5. APPARATUS FOR THE DETERMINATION OF THE THERMAL CONDUCTIVITY OF METALS AND ALLOYS

Most text-books in approaching the question of the thermal conductivity of metals deal at length with Forbes' method. I think the procedure introduces unnecessary difficulties into the subject and it would be better to approach the question from another angle. Forty years ago Berget described a guard tube method for the determination of the conductivity of metals and such a device greatly simplifies the theory of the method.

Take the case of the determination of the conductivity of a single crystal of aluminium with the apparatus shown in Fig. 10. The method of experiment is one in which a longitudinal heat flow is set up in a cylindrical bar 1.4 cm. in diameter and heat loss from the sides is prevented by the use of a guard tube, which in this case takes the form of a coaxial shield. The same gradient of temperature is maintained along the bar and the shield.

It is possible to dispense with one of the two heating coils and simply attach both specimen and guard tube to a cylindrical block containing a heating coil. This procedure simplifies the work, as the hot and cold ends of both the specimen and the guard tube are automatically maintained at temperature equality. In this particular apparatus the gradient in temperature along the coaxial tube was adjusted



to equality with that along the crystal by the aid of two thermocouples attached to the surface of the tube in positions corresponding to the two thermocouples on the aluminium crystal. The space between the aluminium crystal and the guard tube was filled with sil-o-cel, a very light powder of low thermal conductivity. The exterior surface of the guard tube was lagged with magnesia asbestos. The flow calorimeter was attached to the end of the crystal by Wood's metal.

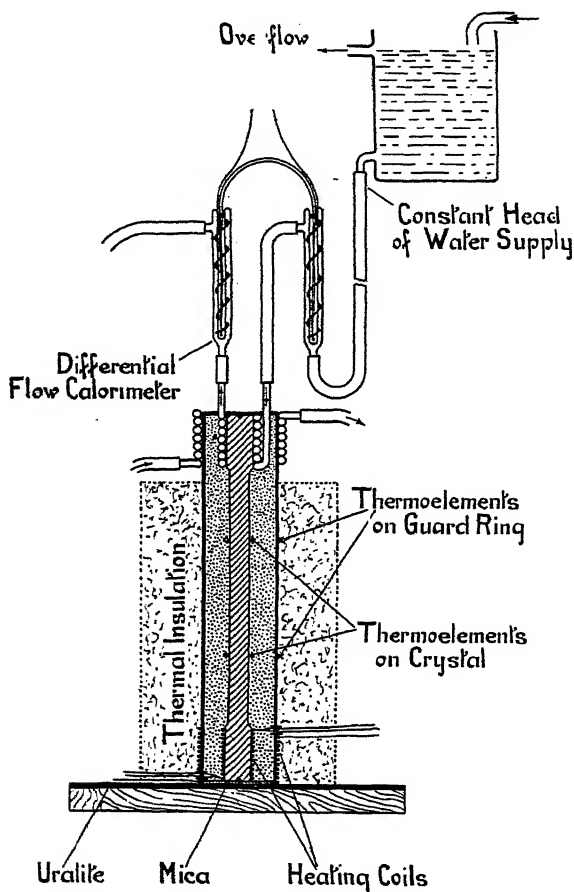


Fig. 10. "Guard tube" apparatus for tests on metal bars.

Specimens of as large a cross-sectional area as practicable should be selected. Although in the present instance the difficulties of making single crystals limited the diameter to 1.4 cm. in the experiments on bronzes and steels, bars up to 3.8 cm. diameter have been used.

The apparatus shown at the bottom of Fig. 11 was used by Mr Schofield and the writer to determine the conductivity of some aluminium and bronze alloys employed in the construction of zero engines. Both the thermal and electrical conductivities are measured at various temperatures in the range  $80^{\circ}$  to  $300^{\circ}$  C.

and the significant fact which emerged from the analysis of the results was that, with one or two exceptions, including notably the high silicon alloy, the Lorenz

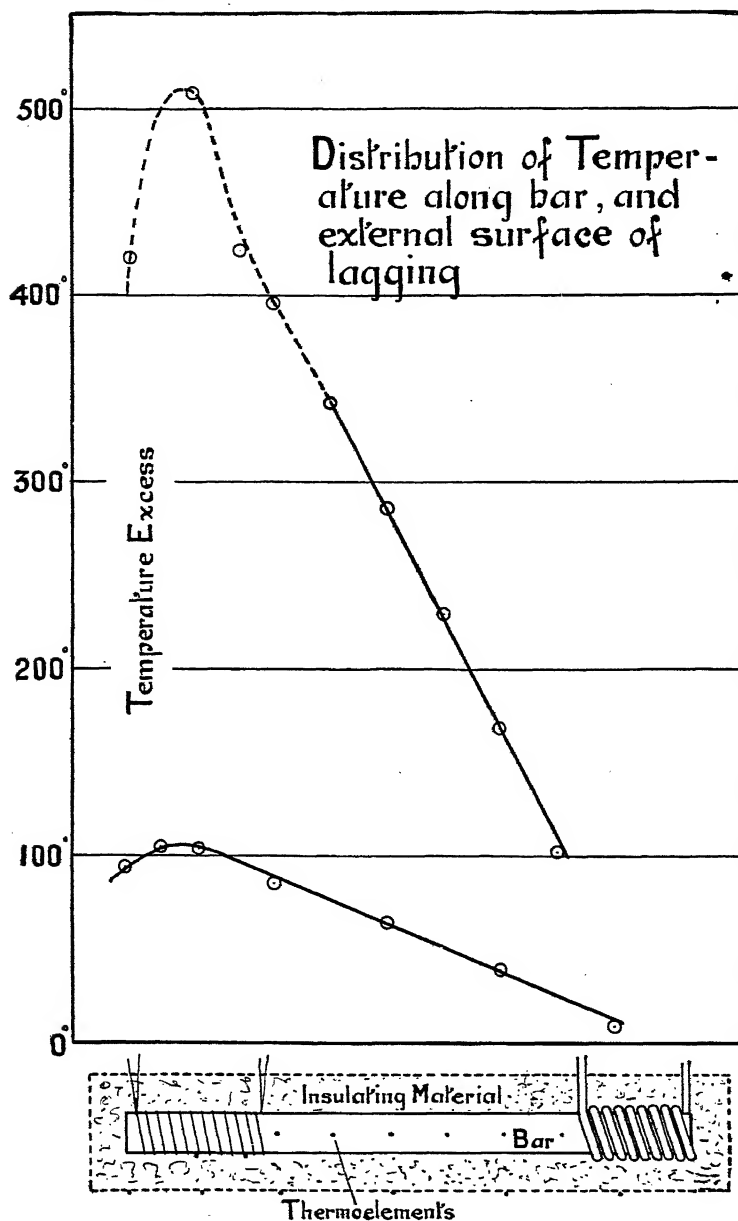


Fig. 11.

law\* applies approximately to the data obtained with these alloys. Furthermore it was found that the two groups of alloys had values of the Lorenz coefficient

\* This law states that the function  $k/\lambda T$  is approximately constant, where  $k$  is the thermal conductivity,  $\lambda$  the electrical conductivity and  $T$  the absolute temperature.

approximating to the values for the pure metals which formed the principal constituents, namely 5.5 for the aluminium alloys and 5.9 for the copper alloys. It is frequently stated in the literature of the subject that the Lorenz law fails when applied to data obtained on alloys. As a generalization this statement appears to be erroneous, and it is not improbable that the thermal conductivity data upon which it is based were unreliable.

It is well to point out that the values of the thermal conductivity of pure metals have not yet been finally settled. Purity of the material exerts a profound influence on the result, and the variations in Table 2 are to be ascribed to this cause, except in the case of Angell's results for high temperatures. He used a novel method: a stout bar was heated electrically and the temperature gradient from axis to surface was observed. In the case of aluminium it was too small to be measured accurately and furthermore longitudinal conduction disturbed the flow.

Table 2: Lorenz Coefficient for Aluminium

Authority	Purity of material % Al	Thermal conductivity at 100° C.	Lorenz coefficient $\times 10^{-9}$				
			18°	100°	200°	300°	400°
Lees ... ..	99	—	5.1	—	—	—	—
Jaeger and Diesselhorst	99	0.49	5.2	5.4	—	—	—
Angell... ..	99	0.49	—	5.4	6.4	7.6	9.1
Konno ... ..	—	0.50	5.5	5.4	5.5	5.4	5.3
N.P.L. ... ..	99.7	0.53	—	5.3	5.6	5.8	6.0
„ ... ..	99.75	0.55	—	—	—	—	—
„ ... ..	Single crystal	0.55	5.4	—	—	—	—

*Apparatus for the determination of the electrical conductivity of the alloys*

It is essential to use the same specimens in the measurements of both thermal and electrical conductivities. In the study of the aluminium and bronze alloys the method used by Mr Schofield and the writer for the electrical measurement consisted in a comparison of the drop of potential across a measured length of the specimen with that across a standard resistance arranged in series with it, when a steady current of the order of 20 amp. was passed through the two. Into the specimen were pegged two thermocouples of copper-constantan, which served not only to measure the temperature but as potential leads for the resistance measurement. By appropriate switching arrangements the thermocouple wires could be rapidly altered so as to serve either purpose, as required. Since any temperature difference between the two ends of the bar would give rise to a thermal e.m.f. when measuring the p.d. across the bar, readings of the latter were obtained for the two directions of the current, so that, by taking the mean of these values, the effect of the thermal e.m.f. was eliminated. Effects, similar in character though smaller in magnitude, occurred in the potentiometer circuit itself and were corrected for by reversal of the potential leads and the leads supplying the current to the instrument.

Particulars of the apparatus are shown in Fig. 12. In order to economize time in testing the specimens, six were placed at once in the furnace, arranged in three pairs. As will be understood from Fig. 12, the three pairs of specimens, of which two pairs are shown, were contained inside a steel tube, and were separated from the tube and from each other by cross-pieces of "mabor" brick, through which their connecting leads passed. These leads were of copper 0.5 cm. in diameter, and were screwed into the ends of the specimen. The thermocouples, which were pegged into the bars, also passed through the mabor pieces. The assembled unit, consisting of the iron tube and its contents, was pushed into the furnace made up

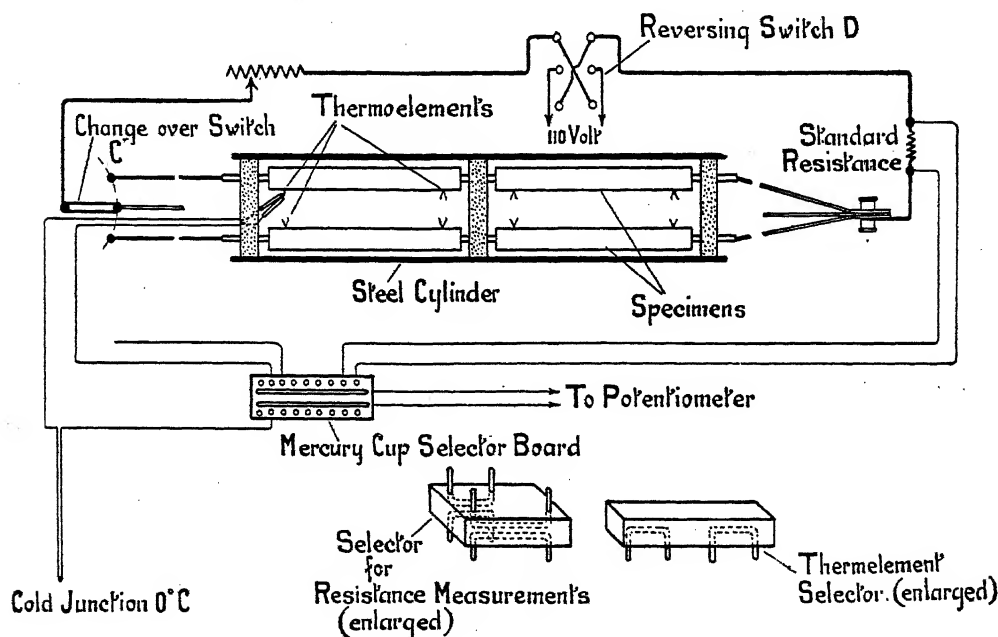


Fig. 12. Apparatus for measuring the electrical conductivity of alloys at high temperatures.

of a refractory tube 6 ft. long, which was wound with nichrome wire and well lagged. Auxiliary heaters of fireclay, wound with nichrome, were inserted into each end of the furnace. By appropriate adjustment of the three heating elements, a reasonable uniformity of temperature could be obtained inside the iron tube containing the specimens. The details of the electrical connections to the specimens are shown in Fig. 12. The change-over switch *C* allowed the steady current of 20 amp., supplied by a battery, to be passed through any one of the three pairs of specimens. This current could be reversed by the switch *D*. The potential leads from the standard resistance, and the thermocouple leads from the specimen, were connected to a mercury cup selector board, and thence to a potentiometer. When the thermocouple wires were used as potential leads for the resistance measurement, the selector block, which is shown (enlarged) near the bottom of Fig. 12, was employed. This consisted of copper rods mounted in ebonite. By insertion of the

pins on one side or the other of this block into the mercury cups, the connections of the potential leads from the specimens could be reversed; while, by the turning of the selector through  $180^\circ$  in the horizontal plane, either the pair of copper wires or the pair of constantan wires, forming the two thermocouples attached to the specimen, could be used as potential leads. When the thermocouple wires were being used for measurement of temperature, instead of resistance, the other selector shown in Fig. 12 was employed.

In determining the resistivity the usual procedure was to make measurements at a series of rising temperatures and to repeat the process until a steady state had been reached. The effect of this treatment on some of the alloys was to produce changes in structure, and the stable state was only attained after several heatings. Other alloys which had been thoroughly annealed gave very consistent results from the beginning. The measurements of thermal conductivity were made after the specimens had attained the steady state, as shown by the electrical measurements.

*Discussion of results obtained in the study of the bronzes,  
and a comparison with previous work*

The main constituent in this series of alloys was copper, and a detailed analysis is set out in Table 3.

Table 3: Bronze Alloys

No. of bar	Percentage composition					
	Tin	Zinc	Phosphorus	Manganese	Aluminium	Copper. Remainder
1	5.0	2.0	0.15	—	—	92.8
2	10.0	2.0	0.15	—	—	87.8
3	8.0	—	0.30	—	—	91.7
4	0.5	38.5	—	0.30	—	60.7
5	10.0	2.0	—	—	—	88.0
6	—	—	—	—	10.0	90.0
7	12.4	—	0.4	—	—	87.2

Except in the case of alloy No. 4, which contains 38.5 per cent. of zinc, the total percentage of constituents other than copper has varied only from 7 to 13. Yet this comparatively small amount of dilution has produced a very marked effect on the conductivity, for whereas the value for pure copper at atmospheric temperature is 0.92 c.g.s., the corresponding values for the alloys range from about one-fifth to one-tenth of this amount.

Dealing first with the effect of tin, which is the most common constituent of the alloys, we may note that a comparison with the present series of experiments is afforded by the work of Lees\*, of Grossmann†, of Schenck‡, and by a previous

\* *Phil. Trans. Roy. Soc.* 208 A, 381-443 (1907).

† *Beibl. Ann. Physik*, 29, 4, 178-181 (1905).

‡ *Ann. Physik*, 32, 261 (1910).

test carried out by us (see Table 4). Approximate corrections have been applied to the values, where necessary, to reduce them to a common temperature of 20° C., and the results have been arranged in the table in order of the tin content of the alloy, an indication being also given of the amount of phosphorus present.

Table 4

Date	Authority	Percentage of		$k_{20}$
		Tin	Phosphorus	
1908	Lees	0	0	0.918
1910	Schenck	5.0	0	0.172
1924	N.P.L. (No. 3)	8.0	0.3	0.108
1905	Grossmann	10.0	0	0.106
1920	N.P.L.	10.0	A small amount	0.100
1924	N.P.L. (No. 7)	12.5	0.4	0.087
1905	Grossmann	25.0	0	0.060
"	"	75.0	0	0.145
"	"	90.0	0	0.132
"	"	100.0	0	0.143

The above values are shown graphically in Fig. 13, which gives the relation between the tin content and the thermal conductivity. A thick line is drawn through the experimental points when they are not widely separated, according to percentage composition; and a dotted line, arbitrarily drawn, is used for the larger gap between the points representing 25 and 75 per cent. of tin. It will be seen that there is a satisfactory agreement between the various determinations.

In addition to the bars Nos. 3 and 7, results for which are included in the above table, bars Nos. 1, 2, 5 contain tin, but with an addition of 2 per cent. of zinc in each case. It will be observed from Table 5 that the conductivities of these bars do not differ very greatly from values to be expected from the tin content as read off from the curve in Fig. 13.

Table 5

Specimen bar No.	Percentage of			$k_{20}$	
	Tin	Zinc	Phosphorus	Observed	Estimated from tin content
1	5	2	0.15	0.188	0.17
2	10	2	0.15	0.101	0.10
5	10	2	—	0.115	0.10

A comparison of the observed values for bars Nos. 2 and 5, which are identical in composition except for a small amount (0.15 per cent.) of phosphorus, appears to show that the presence of the latter in minute quantities produces a very appreciable lowering of the conductivity. The figures for the two bars over the complete range from 75° to 250° C. differ on the average by 0.013 c.g.s., or by about

10 per cent. (see Fig. 14). In confirmation of this view of the effect due to phosphorus, it may be mentioned that according to Pfeleiderer\*, the conductivity of copper at 30° C. (0.93 c.g.s.) was lowered to 0.25 and 0.12 respectively by the presence of 0.63 and 1.98 per cent. of phosphorus.

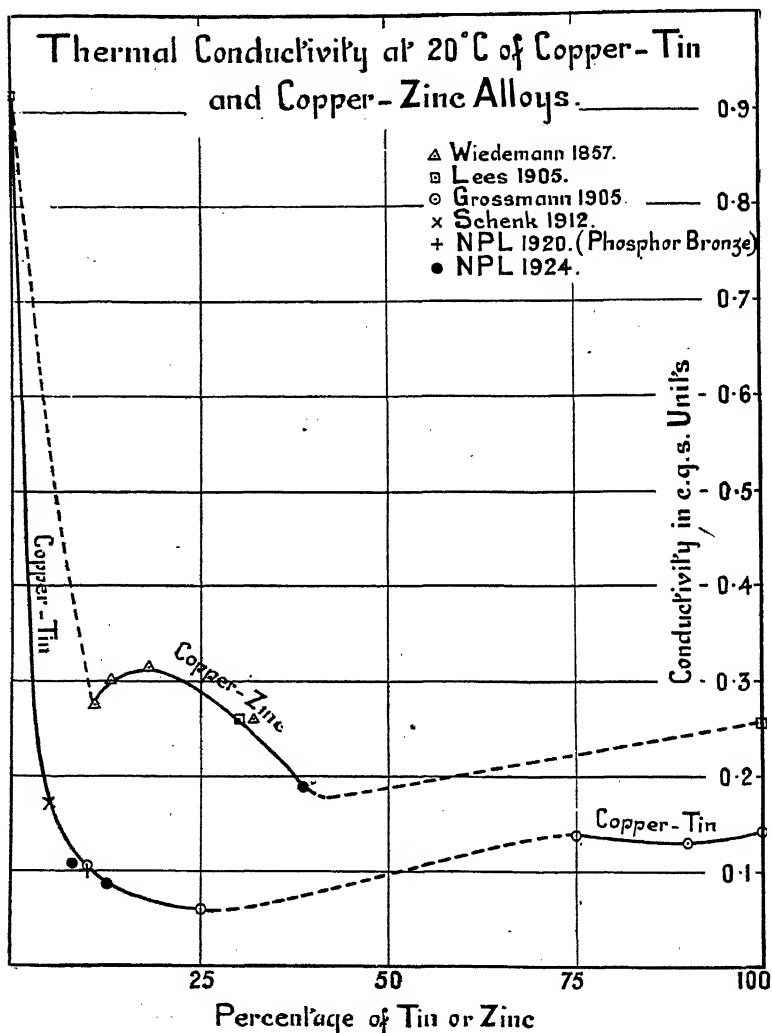


Fig. 13.

Two other alloys remain to be considered (Nos. 4 and 6). For a comparison with No. 4 the values obtained by Lees for brass (30 per cent. zinc), and by Wiedemann† for alloys containing 11, 13, 18 and 32 per cent. of zinc, are given in Table 6, and are plotted in Fig. 13. The figures of Wiedemann date from

\* *Ges. Abhandl. Kenntniss der Kohle*, 4, 409 (1919).

† Landolt, *Phys. Chem. Tab.* (5th edition), 2, 1295 (1923).

1857, and should be accepted with some reserve. A curve has been drawn through all the values, but, for the reason stated, no special significance is to be attached to the inflection which it shows. The dotted portion of the curve is arbitrarily drawn and merely serves to connect points belonging to the same series.

Table 6

Authority	Percentage of zinc	$k_{20}$
N.P.L. (No. 4)	38.5	0.188
Lees, 1905	30.0	0.260
Wiedemann, 1857	11.0	0.275
"	13.0	0.301
"	18.0	0.313
"	32.0	0.260

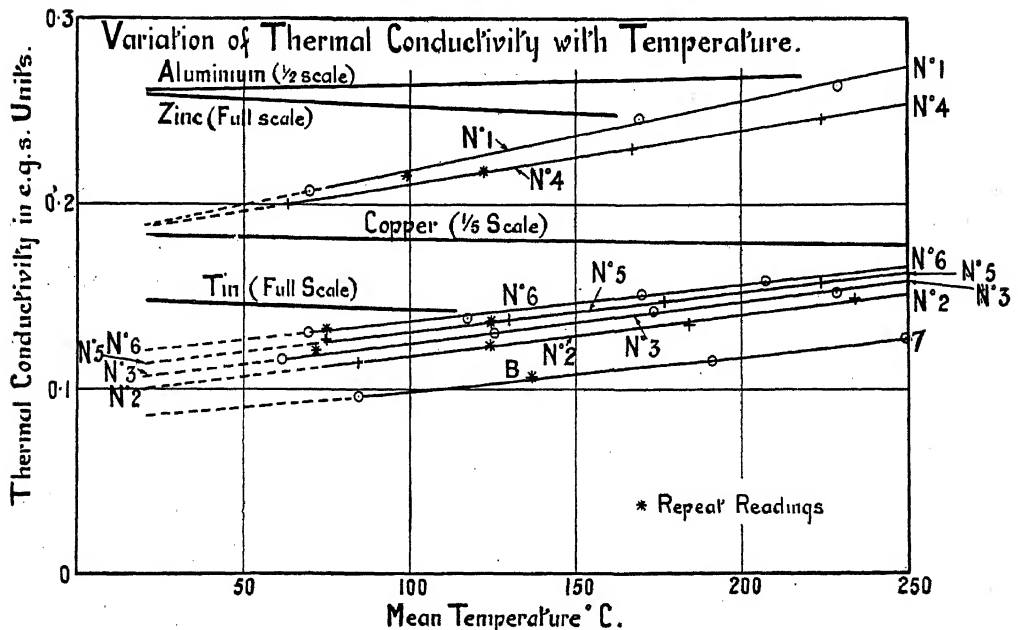


Fig. 14. The numbers denote the bronze alloys whose composition is given in Table 3.

For alloy No. 6 containing 10 per cent. of aluminium, no parallel figures have been traced, but it is perhaps worthy of note that the lowering of the conductivity of copper due to an admixture of 10 per cent. of aluminium is comparable with that due to the same amount of tin.

The above discussion has been concerned with the thermal conductivities of the alloys at one temperature (20° C.). The variations of conductivity with temperature are shown graphically in Fig. 14. For purposes of comparison the values for the pure metals composing the alloys are also indicated. It will be noticed that, whereas the variation of the pure metals is small, being on the whole negative



with rising temperature, the alloys show somewhat large positive coefficients. The aluminium crystal studied (99.6 per cent. Al, 0.2 per cent. Si, and 0.2 per cent. Fe) has a slight positive temperature coefficient—see Fig. 15. In all cases the relation between conductivity and temperature is approximately linear.

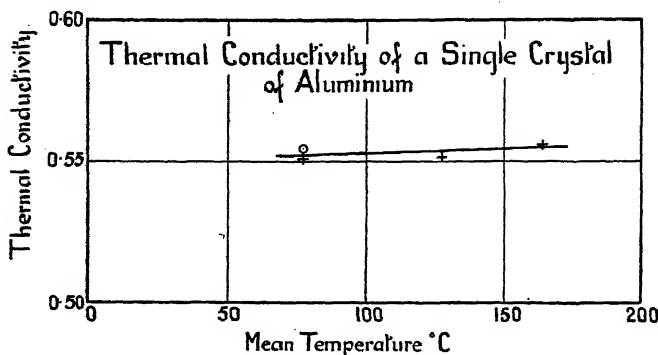


Fig. 15.

*Relation between thermal and electrical conductivities for the bronze and aluminium alloys*

The relation of the conducting powers of pure metals for heat and electricity has for a long time engaged the attention of physicists. In 1853 Wiedemann and Franz propounded a law to the effect that the ratio of the thermal and electrical conductivity was a constant for all metals. In 1872 Lorenz sought to prove, both on theoretical and experimental grounds, that this ratio was proportional to the absolute temperature. On the development of the electron theory of conduction, Drude, H. A. Lorentz, and J. J. Thomson have independently arrived at the same conclusion as Lorenz. The experimental evidence available up to 1900 was not sufficiently reliable to allow a definite confirmation of the theory. In that year Jaeger and Diesselhorst published the result of their investigation, which gave directly the ratio of the two conductivities for a number of pure metals over the range from 18° to 100° C. They showed that the value of the function  $k/\lambda T$  (Lorenz's constant) was nearly constant over this range, and did not vary greatly from metal to metal. In 1905 Lees obtained a close agreement with the values of Jaeger and Diesselhorst at 18° C., and carried the investigation down to -170° C. Down to -100° C. the value of the function showed, on the whole, a slight tendency to decrease, while below -100° C. the decrease became more marked, and wide divergencies appeared among individual metals. Summarizing the position as regards the pure metals, it may be said that from -100° C. to +100° C., and probably to much higher temperatures, the function\*  $k/\lambda T$  does not vary greatly in value from metal to metal and is nearly constant, showing a slight tendency to increase with temperature.

\* In view of the fact that the function  $k/\lambda T$  is not an absolute constant, it would be preferable to use the term coefficient for the numerical value appropriate to particular metals and groups of alloys.

The position as regards alloys is not so clearly defined, since the very wide field of investigation which they present has hitherto hardly been explored at all.

The mean value of Lorenz's coefficient for all the copper alloys now under consideration, together with the percentage difference between the extreme values, is set out in Table 7.

Table 7

Temperature °C.	Lorenz's constant, $k/\lambda T$	
	Mean value for all the bronze specimens	Percentage difference between extreme values
20	$[6.1_5] \times 10^{-9}$	6
75	$5.9_2$	5
100	$5.8_7$	4
150	$5.7_9$	2
200	$5.7_8$	2
250	$5.8_1$	2

*Note.* The value at 20° C. is obtained by extrapolation.

As regards the range covered by experiment (75° to 250° C.), it appears that the mean value of the function  $k/\lambda T$  is practically constant, and that the extreme range of values for all the bronze bars does not exceed  $\pm 2.5$  per cent., an amount which is probably within the limits of experimental error. As to the absolute value of the function, it is to be noted that Jaeger and Diesselhorst's mean value for eight pure metals at 20° C. and 100° C. is approximately  $5.7_5$ . Lees gives a similar value for the pure metals at 20° C., while his value for brass (which corresponds to alloy No. 4) is  $5.8_3$ . I have studied a single crystal of very pure copper and obtained the value  $5.8_9$ .

A comparison is also afforded by the work on the copper-tin alloys of Grossmann, whose values are set out in Table 8.

Table 8

Tin content (%)	Value of $k/\lambda T$
10	$5.9_5 \times 10^{-9}$
25	$6.3_8$
75	$5.6_3$
90	$5.4_0$
100	$5.8_8$

The conclusion, which has been reached above, that all the bronzes under investigation obey Lorenz's law of the relation between thermal and electrical conductivity, has a practical bearing in that it means that the thermal conductivity could be deduced from a measurement of the electrical conductivity. The determination of this latter constant presents far less difficulty than that of the former, so that, if the assumption be made that Lorenz's law applies to other alloys of an analogous nature, their thermal conductivities could be deduced with comparative

ease by the method indicated. Since the temperature coefficients of thermal conductivity for the alloys do not differ very markedly, a rough value at any temperature could be obtained from a single measurement of electrical conductivity at atmospheric temperature, but a better approximation would be obtained if the electrical conductivity were determined at the appropriate temperature.

As regards the Lorenz coefficient for the aluminium alloys, with the exception of the 13 per cent. silicon alloy, the 21 alloys give very consistent results\*, the mean values being as follows:

Table 9

Temperature (° C.)	Lorenz coefficient
80	$5.31 \times 10^{-9}$
150	5.38
200	5.49

A determination of the Lorenz coefficient for a single crystal of aluminium (99.6 per cent. aluminium) gave the value  $5.46 \times 10^{-9}$ , which is in good agreement with the mean value for this group of alloys, with the exception of the 13 per cent. silicon alloy. It will be observed that the Lorenz coefficient for the aluminium alloys is decidedly lower than the value for the copper alloys.

#### § 6. ACKNOWLEDGMENTS

I desire to record my indebtedness to the Council of the Royal Society for permission to reproduce diagrams from a paper published in the *Proceedings*, Vol. 104, and entitled "The Measurement of Thermal Conductivity" (Griffiths and Kaye) and for the loan of blocks illustrating a paper published in the *Proceedings*, Vol. 115, and entitled "The Thermal and Electrical Conductivity of a Single Crystal of Aluminium" (Griffiths).

I am also indebted to the Council of the Institute of Metals for permitting electrotypes of some diagrams and abstracts to be made from a paper published in the *Journal*, Vol. 39, and entitled "The Thermal and Electrical Conductivity of some Aluminium Alloys and Bronzes" (Griffiths and Schofield); and to the *Journal of Scientific Instruments* for the loan of the blocks of Figs. 2, 4, and 8.

#### DISCUSSION

Dr G. W. C. KAYE: I wish to support Dr Griffiths' plea that methods which are primarily of historical importance should not be given the premier place when the principles underlying the measurement of thermal conductivity are taught. [The speaker then gave some results which he and Mr Higgins had obtained by the divided bar method on quartz crystal cut parallel and perpendicular to the axis.]

\* Since this work was completed a paper by Masumoto, *Sci. Rep. Tôhoku Imp. Univ.* 13, 229 (1925), has come to my notice which deals with some eighteen aluminium alloys. His data indicate that the mean value of the Lorenz coefficient is  $5.4 \times 10^{-9}$  at 30° C., which is in satisfactory accord with the above data.

As regards the electrically heated plate method, it has the additional advantage of being convenient for exploring the variation of thermal conductivity with temperature. The true conductivity is obtained by jacketing the entire apparatus in a constant temperature enclosure and working with only small differences of temperature between the hot and cold plates. [The speaker illustrated this point by showing results for single bismuth crystals, water, various oils and solid and liquid sulphur.]

Mr F. H. SCHOFIELD dealt with the application of the method of conformal representation to a problem mentioned by Dr Griffiths—namely, the heat flow from a thin plate embedded in a mass of poorly conducting material, which is contained within a rectangular isothermal boundary. He gave an expression for the “edge correction” for such a plate and showed a diagram of the calculated distribution of flow lines and isothermals within the material.

Mr J. H. AWBERY: I think the date is far distant when the theory of conformal representation will be capable of generalisation for solving problems in three dimensions. This is not to say that such problems are at present insoluble, but the method referred to—which is merely one form of the method of conjugate functions—is hardly likely to be applicable to them. We are accustomed to the idea of conformal transformations, in which one surface, say that of a sphere, is applied to another. In using the method for potential problems, we apply a polygon or other figure to a square, so that there is a one-one correspondence between points in the two figures. For a spatial problem, it would be necessary to transform a solid figure to a cube. The equations would be

$$x' = f_1(x, y, z); \quad y' = f_2(x, y, z); \quad z' = f_3(x, y, z).$$

The advantage possessed by the plane is that these equations become one, instead of two, with one variable only. In fact the new complex variable  $(x + iy)$  is related to the old by one equation  $(x' + iy') = f(x + iy)$ . The method is only made possible by the dissymmetry between  $i$  and  $1$ , a dissymmetry not shared by the three unit vectors in space.

Turning to the questions suggested by the lecturer in regard to the Lorenz function, I would ask whether we have real grounds for expecting a constant at all? Mica, sulphur and other non-metals have a thermal conductivity which is not infinitely small compared with metals, and this suggests that the atoms, as opposed to the electrons, must play some part in the thermal conductivity, although not in the electrical. After all, theory discusses only the relation between the electrical conductivity and the thermal conductivity due to the electrons, considered in the old theory as a perfect gas, and in the new one as a degenerate gas, whilst experiment gives the total conductivity. The idea that the metallic part ( $\lambda_m$ ) and non-metallic part ( $\lambda_i$ ) of the thermal conductivity could be separated occurred to Gruneisen and Goens\*, but, if I have read them correctly, they make a curious

\* *Zs. für Phys.* 44, 615 (1927).

error in the treatment of the very valuable data which they give. They consider that the thermal *resistance* is additive, so that the total resistance is made up of that due to the electrons, and that due to the atoms. With the substitution of conductivity for resistance, I think their method will be very valuable. They give data for a number of specimens of differing purity, and if the thermal conductivity be plotted against the electrical conductivity, the various specimens give points along a curve. This curve can be extrapolated to the point where the electrical conductivity is zero, and it will be found that this point is not at the origin. When the electrical conductivity ceases, so that electrons are presumably taking no part in the phenomena, there is still a finite thermal conductivity. I would suggest that this residuum is  $\lambda_e$  and that if it were subtracted from each observed  $\lambda$  so as to give  $\lambda_m$  we should find that  $\lambda/\sigma T$  was much more nearly constant. On this view, the constancy of the Lorenz coefficient for a series, say the aluminium series, of alloys is comprehensible. Whilst the alloy remains rich in aluminium,  $\lambda_e$  is small compared with  $\lambda_m$ , so that the coefficient is nearly the theoretical one.

All the above argument really supposes a homogeneous medium. In the case of a metal made up of separate crystals, it may be that there are temperature discontinuities at the faces, although this is not certain. It is also possible that in alloys there is a counter e.m.f. proportional to the current, and therefore indistinguishable from a resistance; there would be no counterpart to this in the thermal conductivity, so that Lorenz' coefficient would again be altered. This idea was worked out by Rayleigh\*.

MR R. W. POWELL: I was pleased to hear Dr Griffiths refer to some of the variations which are found in the values of the Lorenz constant for different metals, and in view of the theoretical interest attached to this function I would like to emphasise the importance of combining a measurement of electrical conductivity with that of thermal conductivity. Dr Griffiths has shown us an example in which the thermal conductivity of the metal under test varied according to its previous heat treatment, from which we see that the two conductivities should be measured simultaneously in order to give the correct value for the Lorenz constant.

I would also like to mention that Worthing† has determined the Lorenz constant for carbon, in the form of an electrically heated filament, and has found that the value decreases from  $2.8 \times 10^{-8}$  ohm-calorie units at  $1700^\circ$  absolute to  $2.1 \times 10^{-8}$  ohm-calorie units at  $2100^\circ$  absolute. The Lorenz constant for carbon thus appears to have a value about four times that for the metals, and decreases with increasing temperature, whereas the opposite change appears to be indicated with metallic conductors.

MR S. SKINNER: I feel that we are much indebted to Dr Ezer Griffiths for a very complete account of the methods for measuring thermal conductivities at the National Physical Laboratory, and I think we now have accurate values of the thermal conductivity and of the temperature coefficients for many materials used

\* *Nature*, 54, 154 (1896).

† *Phys. Rev.* 4, 535 (1914).

in the arts for heat insulators and other purposes. This was badly required, as anyone may see who examines the older text-books. It is a feature of the methods that great pains have been taken to make the conditions thoroughly definite, which was not the case with many of the older methods. The analogy between heat conduction and the flow of electrical currents is of great use. I look forward to further good results from the continuance of these measurements.

DR ALLAN FERGUSON: I am sure that we have listened to Dr Griffiths' critical address with both pleasure and profit—he has given an admirably clear account of a successful attack on a subject which bristles with experimental difficulties. I should like to take up the cudgels in defence of Forbes' memory—his method, perhaps unduly exalted in the past, is liable to a period of undue depreciation. But it stands as a highly ingenious attempt to obtain absolute values for  $K$  at different particular temperatures which shall be quite independent of any assumptions concerning the variation of conductivity with temperature. If we consider any cross-section at a temperature  $\theta$  on a long bar, the conductivity  $K$  at that temperature is unambiguously determined if we know the sectional area and temperature at the point in question and the rate of flow of heat across the isothermal surface at this point, assumed plane. This last quantity is of course obtained from the "dynamical" experiment, which may not be above criticism. *A propos* of such experiments, it would be very helpful to have Dr Griffiths' opinion of the "five-fourths" power law of radiation, inasmuch as this law enables one to obtain a solution of certain of the conductivity equations which is valid over a range considerably wider than is usually assumed possible. In my own experience, a plot of  $\theta^{-\frac{1}{4}}$  against the time yields a curve which is rectilinear over a surprisingly wide range. A number of the methods described eliminate side losses as much as possible, and we should welcome remarks from Dr Griffiths' dealing with the relative merits of methods which seek to *eliminate* these losses and of those methods which seek to *determine* these losses on the basis of the  $\frac{5}{4}$ ths or some other suitable law of radiation.

Where Dr Griffiths has given so much it seems selfish to ask for more, but there is a large class of experimental methods which Dr Griffiths has but touched upon. I refer to those methods in which the conductivity equation is integrated over a suitable range of temperature—usually with simplifying assumptions concerning the variation of conductivity with temperature. Examples of such methods are afforded by two concentric spherical surfaces or two coaxial cylinders maintained at temperatures  $\theta_1$  and  $\theta_2$  respectively.

Lord Kelvin was wont to speak enthusiastically of Ångström's method, and one or two experimenters, employing ingenious variations in the method of controlling the heat supply, have lately used it. A few remarks from Dr Griffiths on these methods would add greatly to the value of his already valuable address.

MR T. SMITH: I do not think the suggestion that these problems in three dimensions are insoluble should pass without comment. Much work has been done in recent

years on orthogonal space transformations, and some of the results may be applicable to physical problems. Even if we take the most unfavourable view, and assume that a solution in tabulated analytical functions is unattainable, we can always reach a solution to any desired degree of accuracy by numerical processes. Given a definite problem of this type, such as is of importance in experimental work, a solution, at least as accurate as is significant when experimental errors are considered, can always be obtained in a reasonably short time by the continuous refinement of a crude first approximation. Perhaps the most remarkable fact about such solutions of some problems is the rapidity with which a sufficiently correct solution may be reached.

**THE PRESIDENT:** The treatment and form of the subject of thermal conductivity has changed greatly of recent years. Formerly it was very academic, a source of Fourier and conformal representation problems, and of laboratory experiments like the Forbes' bar experiment. To-day, as can be seen by a glance at the exhibits on the table, the subject has many practical applications. Almost the only industrial problems of the academic days was the flow of heat through boiler plates, and to this the physicist's results were applied timidly. Nowadays refrigeration and other industrial processes call for precise knowledge of materials. Industry has thus compelled the development of new and rapid methods of measurement which, as the lecturer has shown us, can be accurate, simple and beautiful. Provided that the pressure of industrial demands does not overwhelm the study of the abstract side of thermal conductivity, the new conditions are greatly to the advantage of pure physics.

**LECTURER'S REPLY:** Mr Schofield by the application of conformal representation has shown how the edge effect can be calculated exactly; hitherto workers have depended on the method of Fourier analysis for a close approximation. It must be pointed out, however, that his solution applies to the case of an infinitely long strip but not to a circular plate or to the heat leakage at the four corners of a rectangular plate.

I agree with Mr Skinner that electrical methods, such as the determination of the capacity of a condenser of appropriate form, can be employed for ascertaining the coefficient in calculations of heat flow for geometrical forms too complicated to tackle mathematically.

It is gratifying to hear from Mr T. Smith that some of the problems mentioned in the lecture might be amenable to solution by approximate methods giving any desired degree of accuracy.

In spite of Dr Ferguson's defence of Forbes' method, I am afraid I am still of opinion that any merit it may possess lies in its potentialities as an examination question. As regards the five-fourths power law for heat loss by convection, it appears to hold good for natural convection when there are no draughts. This is a subject I am now studying in connection with heat transmission to or from pipes in an air stream. In the methods indicated by Dr Ferguson the differences of

temperature are comparatively small and it suffices generally to assume a linear variation of conductivity with temperature, which will usually yield a simple formula. I have not referred specifically to methods employing coaxial cylinders or concentric spheres, since it seems to me that the theoretical advantages obtained by the use of such shapes in place of plane slabs and the like are outweighed by the practical difficulties involved.

I greatly appreciate the kind remarks of the President and other Fellows. All I have attempted in the lecture is to indicate the practical difficulties of the worker who has to determine the thermal conductivity of a material in whatever form it may be supplied to him.





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## THE PHOTOGRAPHIC MEASUREMENT OF THE RELATIVE INTENSITIES OF THE $L_{\alpha_1}$ , $\alpha_2$ , $\alpha_3$ LINES OF SILVER

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**ABSTRACT.** A knowledge of X-ray line intensity is needed in the theory of atomic structure and in chemical analysis by means of X-rays. The relative advantages of the ionization, Geiger counter, and photographic methods of measurement are discussed. The advantages of the photographic method are that (1) a permanent record is obtained, and (2) the photographic effect is cumulative, a condition which is especially valuable for lines of weak intensity. Its disadvantages are the difficulty of deducing the intensity from the blackening of the emulsion, and the care needed in development and photometry. The ionization method requires a steadier source of radiation, and difficulties arise owing to "end" effects, Compton scattering, and internal absorption of characteristic X-rays. The Geiger counter method counts the quanta, but the unjustifiable assumption is made that the number of electrons ejected from a metal foil by X-rays, on the side of incidence, depends only on the number of incident quanta. In the photographic method used by the author the densities,  $D$ , of the photographic images of the lines, produced by a vacuum spectrograph, are measured by means of a Moll micro-photometer. The density is a function of the exposure, the frequency, the photographic emulsion, and the development. This function is discussed. Previous work has shown that the Bunsen-Roscoe reciprocity law applies in the case of X-rays, and it is shown that for constant development, and for the range of frequencies measured,  $D$  is a function of  $Nt$ , where  $N$  is the number of quanta absorbed per second in the emulsion and  $t$  the exposure time. This function is found by varying  $t$ . Corrections are made for the overlapping of the lines. The results obtained are:  $L_{\alpha_1} : L_{\alpha_2}$ , 100 : 12.0;  $L_{\alpha_1} : L_{\alpha_3}$ , from 100 : 4.6 to 100 : 7.3, according to the tube voltage. A value of  $L_{\alpha_1} : L_{\beta_1}$ , of less accuracy, is found as 100 : 40.

### § 1. INTRODUCTION

A KNOWLEDGE of the relative intensities of lines in X-ray spectra is necessary for the verification of the many theories of the atom which have recently been put forward. Further, in an investigation which has recently been made in this laboratory of chemical analysis by X-rays it has become evident that if that method, which has been found to be highly sensitive, is to be made quantitative, a knowledge of X-ray line intensities and particularly of the "photographic" intensities is essential.

### Definition

In this paper the intensity of an X-ray line of frequency  $\nu$  is defined as the number of quanta of *characteristic* radiation of this frequency (general radiation being thus excluded) which proceed per second from the anticathode in the X-ray tube.

### Methods of measurement

Three methods have been employed in measuring the intensity of X-ray lines. All these depend upon a secondary effect of the X-rays, namely the ionization produced by the photo-electrons ejected by the X-rays in some material.

The ionization method, developed chiefly by Duane and his collaborators\*, is the method most frequently employed. Here the photo-electrons are ejected from a gas in which the X-radiation is absorbed and the current thus permitted to pass is registered.

In Jonsson's method† the photo-electrons ejected from a metal foil are counted by Geiger's device.

In the photographic method the photo-electrons ejected in the emulsion render the silver halide grains developable. This method, as applied to X-ray intensities, owes its development chiefly to Friedrich and Koch‡, Glocker and Traub§, Allen and Laby||, and Bouwers¶, and has been applied to the measurement of relative intensities of lines by Siegbahn and Zacek\*\*.

The advantages of the photographic method are that (1) a permanent record is obtained; (2) the photographic effect is cumulative. This condition is especially valuable in the case of lines of very small intensity, and it averages out short-period variations in the intensity of the source.

The disadvantages of the method are (1) the difficulty of deducing the intensity of the X-rays from the blackening they produce in the photographic emulsion; (2) the care necessary in photometry; and (3) the care necessary in development.

The disadvantages of the ionization method are as follows: (1) Very steady sources of X-rays are needed, except when a balance method is used. (The balance method introduces complexity.) (2) Some of the ionization produced by photo-electrons ejected from the gas in the vicinity of the ends of the electrodes in the ionization chamber is not recorded. Since the manner of distribution in space of the directions of ejection is not satisfactorily known, the necessary corrections cannot be accurately estimated. (3) The relation between the number of photo-electrons and the number of quanta entering the chamber is complicated by

\* Duane and Stenstrom, *Nat. Acad. Sci. Proc.* 6, 477 (1920). Duane and Patterson, *Ibid.* 6, 526 (1920); 8, 89 (1922).

† Jonsson, *Zeits. für Phys.* 36, 426 (1926); 41, 221, 801 (1927); 46, 383 (1928).

‡ Friedrich and Koch, *Ann. der Phys.* 45, 399 (1914).

§ Glocker and Traub, *Phys. Zeits.* 22, 345 (1921).

|| Allen and Laby, *Proc. Roy. Soc. Vic.* 31, 421 (1919).

¶ Bouwers, *Over het meten der Intensiteit van Röntgenstralen: Eindhoven* (1924).

\*\* Siegbahn and Zacek, *Ann. der Phys.* 71, 187 (1923).

Compton scattering and internal absorption of characteristic X-radiations, and thus difficulties arise in determining the relation between the ionization and the number of quanta.

Jonsson claims that the ratio between the (corrected) observations with the Geiger counter and the number of entrant X-ray quanta is a constant independent of the wave-length. This assumption is not justifiable, since the fraction of the electrons ejected below the surface of the foil which actually produce discharges will depend on the mean depth of ejection and hence on the wave-length of the X-rays. Further disadvantages are: (1) the difficulty of obtaining counter needles which discharge for every photo-electron, and give no spurious effects; also the gradual deterioration of such needles; (2) the fact that since it is inconvenient to prolong considerably the time occupied by each observation, the method is less suitable than the photographic for very weak lines.

## § 2. THE PHOTOGRAPHIC METHOD

The density of an element of area of the film depends on the following factors: (1) the function

$$F'(N_1, dt_1, N_2, dt_2, \dots),$$

where  $N_1$  represents the number of quanta of radiation absorbed in the emulsion during the element of time  $dt_1$ , at the commencement of the exposure, and so on,  $dt_2, dt_3, \dots$  being successive elements of time; (2) the frequency  $\nu$  of the radiation; (3) the emulsion; (4) the developer; (5) the time of development; (6) the temperature of the developer. Other factors have a minor influence.

Assuming that the last four of the above factors are constant and such as are found satisfactory in X-ray photography, it follows that

$$D = F''(N_1, dt_1, N_2, dt_2, \dots, \nu).$$

The important case is when  $N$  either is constant during the exposure, or varies in a regular, rapid cycle which has some definite "wave-form," as is the case when all the radiations coming into consideration have the same excitation potential and are excited by means of an alternating potential.

It then follows that

$$D = F(N, t, \nu),$$

where  $N$  denotes the mean value.

In the usual methods of optical spectro-photometry\* the time factor is eliminated, since the exposure times for all lines are the same, a scale of densities being formed along the length of each line by means of a calibrated absorption wedge, and the relative intensities obtained by matching portions of equal density. No determination of X-ray line intensities by this method has, however, yet been reported, the difficulty being the obtaining of suitable wedges.

\* Dobson, Griffiths, and Harrison, *Photographic Photometry*, pp. 28-55; Dorgelo, *Phys. Zeits.* 26, 756 (1925).

For light of given frequency, Kron\* and others† have found certain complex empirical expressions for the function  $F$ , which reduce, for small ranges of intensity, to the Schwarzschild‡ relation:

$$D = F(Nt^p),$$

where  $p$  is of the order of 0.9, the source being steady.

As regards sources with rapid and regular intermissions, the experiments of Weber§ and Howe|| indicate that, provided the total exposure time is constant,

$$D = f(NT),$$

where  $T$  is the portion of the total time during which the radiation was incident on the film. If, as is fairly justifiable, it be assumed that this property applies in the case of X-rays also, it follows that for fluctuating sources the expression

$$D = F(N, t, \nu)$$

applies even if the "wave-forms" for the radiations considered are not identical.

Glocker and Traub¶, and also Bouwers\*\*, have verified the validity of the Schwarzschild law in the X-ray region, using an intermittent source of radiation such as that provided by a transformer with mechanical rectifier. The mean value obtained for  $p$  was 0.98, but within the limits of experimental error the assumption of the Bunsen-Roscoe reciprocity law

$$D = F(Nt) \quad (\nu \text{ being constant})$$

was justified. The maximum ratio of the intensities used was 1 : 9.

The X-ray tube used in the experiments to be described was connected directly to the secondary of a transformer fed with a.c. of 50 cycles per second, the current through the tube being thus a pulsating one similar to that used by Bouwers. It is assumed that the amplitude and form of the pulses used by the author were constant.

Experiments, which will be described later, showed that for silver  $L$  radiation excited in this way the reciprocity law was valid within the limits of experimental error.

In radiation reflected from a rocking crystal, as used in the work to be described, the intensity incident on any element of area of the film varies with the position of the crystal. This causes no error, however, since the reciprocity law is valid. It is worthy of note that the range of validity is likely to be larger than usual, on account of the rapid cyclic character of the variation in intensity.

Berthold†† has examined the relation between the photographic density and the

\* Kron, *Ann. der Phys.* 41, 751 (1913).

† Parkhurst, *Astrophys. Journ.* 30, 33 (1909); Ives, *Ibid.* 31, 157 (1910); Jones and Huse, *Journ. Opt. Soc. Amer.* 7, 1079 (1923); 11, 319 (1925).

‡ Schwarzschild, *Astrophys. Journ.* 11, 89 (1900).

§ Weber, *Ann. der Phys.* 45, 801 (1914).

|| Howe, *Phys. Rev.* 8, 674 (1916).

¶ Glocker and Traub, *Phys. Zeits.* 22, 345 (1921).

\*\* Bouwers, *Over het meten der Intensiteit van Röntgenstralen: Einthoven* (1924).

†† Berthold, *Ann. der Phys.* 76, 409 (1925).

ionization current for several wave-lengths between 0.15 and 1.9 Å.U. He determined, in effect, the relative numbers of quanta of various frequencies the absorption of which in the emulsion produced a given density, thus avoiding reference to blackening laws. His final results are contained in the expression:

$$n \propto \lambda / (15.83 - 1/\lambda), \quad \text{where } \lambda \text{ is in } \text{Å.U.}$$

The measurements of Barkla and Martyn\* of the same relation gave results in fair accord with the above expression.

Bouwers† has compared the photographic density produced spectroscopically by radiations of a few different frequencies with the energy of the incident (filtered) radiation, measured bolometrically. His results, expressed in terms of the number  $n$ , as above, are as follows, the values computed from Berthold's expression being inserted for comparison:

Table 1.

Wave-length (Å.U.)	0.19	0.22	0.47	0.56	0.71
$n$ (Bouwers)	1	1.05	2.22	2.30	2.22
$n$ (Berthold)	1	1.05	1.91	2.22	2.77

The results of Allen and Laby‡ are not directly comparable, since they related to heterogeneous radiation. These authors found that the density produced by the general radiation from a Coolidge tube excited by potentials of 31.5, 73, and 83 kilovolts was proportional to the quantity of electricity which passed through the tube and to the square of the applied potential.

The above results show that, within the limited ranges of frequency used in the experiments to be described, it is justifiable to assume that the density depends on the number of quanta absorbed, but not on the frequency.

The influence of the emulsion and also of the development are of the same nature as for light, and the conditions for optimum development are also the same.

### § 3. EXPERIMENT

A spectrograph with a common vacuum for the spectrograph and X-ray tube, as used by Shearer§ in this laboratory, was employed, the crystal and camera being operated through conical joints as in Siegbahn's|| design. The main features of this apparatus are illustrated in Figs. 1 and 2.

The only features needing comment are (1) a lapped joint at  $D$ , Fig. 2, which allowed the ready removal of the anticathode for cleaning, and accurate re-assembly; (2) a rubber ring  $H$  which permitted the ready adjustment of the orientation of the X-ray tube relative to the spectrograph. The principal slit  $K$  was 0.1 mm. wide and the slit  $M$  about 1 mm.

Spectrograph and X-ray tube were evacuated by separate Gaede diffusion pumps, backed by the same Hyvac pump. A mercury trap, with freezing mixture,

\* Barkla and Martyn, *Phil. Mag.* 25, 296 (1913).

† Bouwers, *Over het meten der Intensiteit van Röntgenstralen: Einthoven* (1924).

‡ Allen and Laby, *Proc. Roy. Soc. Vic.* 31, 421 (1919).

§ Shearer, *Phil. Mag.* 4, 745 (1927).

|| Siegbahn, *The Spectroscopy of X-Rays*, pp. 63-65.

was inserted between the X-ray tube and its pump. Calculations showed that, on account of the high resistance of the slit *K* to the flow of gas at low pressures, a much lower pressure should be obtainable in the X-ray tube than in the spectrograph, where castor oil is present. The steadiness of the running of the X-ray

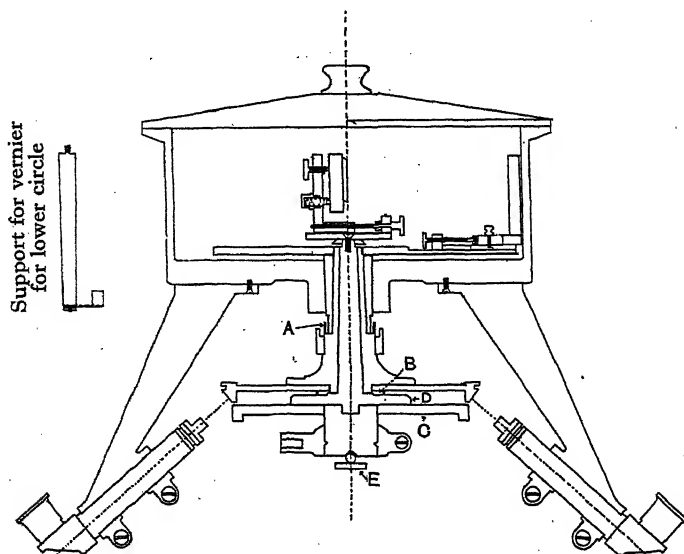


Fig. 1. Sectional side elevation of spectrograph.

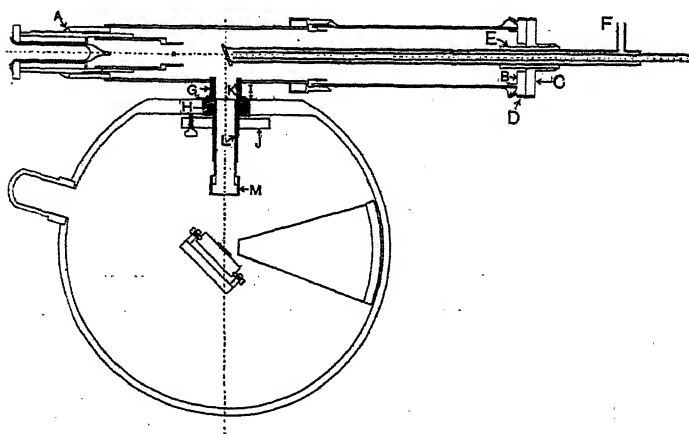


Fig. 2. Sectional plan of spectrograph.

tube indicated a satisfactory vacuum therein and showed the advantage of having two pumps connected as described.

The tube was fed directly from a 20 kv. transformer. Turfsten was first used for the filament, but later a Wehnelt filament proved very satisfactory. A small auxiliary voltage was sometimes applied to the hood in the latter case. Suitable rheostats permitted fine control of the tube voltage and current, the fluctua-

tions of these being of the order of 1 per cent. The crystal was rocked by the usual cam mechanism, the sweep being amply sufficient to cover the reflection angles of all three lines  $L\alpha_1, \alpha_2, \alpha_3$ .

With the tungsten filament, but not with the Wehnelt, a screen of carbon paper covered the end of the camera. Calculations showed that the correction for the different absorptions in this of the  $L\alpha_1, \alpha_2, \alpha_3$  was negligible. A series of exposures was taken on each film (Kodak Radia-tized Dental X-Ray) for times adjusted to give suitable densities for the various lines and to permit the convenient construction of calibration curves as described later. The film was developed for five minutes at 18.7° C. in the solution recommended by the Eastman Kodak Co., these being the optimum conditions specified by them.

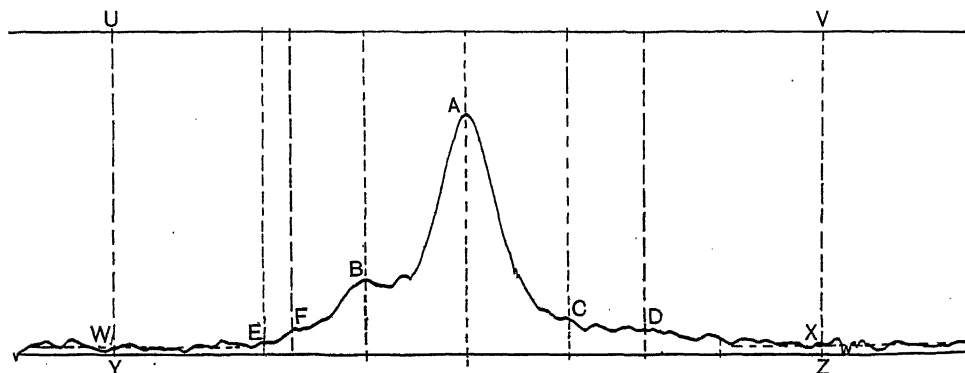


Fig. 3. Photographic photometer record†.

The film was photometered in a micro-photometer of the Moll type. Care was taken that the portions of the various lines photometered had been exposed at the same place in the spectrograph. To eliminate galvanometer lag the speed of translation of the film was made small, namely about 2.5 mm. per hour.

Each photographic photometer record (see Fig. 3) refers to all portions of the film subject to reflected X-radiation during the corresponding exposure. The zero line  $UV$  was determined by running the apparatus with the photometer lamp off for a few minutes immediately before and after the run, a procedure which gave two small sections near  $U$  and  $V$  respectively. For the dupli-tized film used the densities should strictly be obtained from the light incident on and emergent from the "front" emulsion, but since the "back" emulsion is very little affected by the X-rays, which are strongly absorbed in the front emulsion and the celluloid, and since the latter has constant photometric density, the foregoing theory may be applied to the densities of the film as a whole in determining the intensities. The line  $YZ$  represents the light intensity incident on the film during the photometer run. To obtain  $YZ$  observations were made, with a scale replacing the photographic paper, of the densities of the uniform portions of the film on either side

\* Eastman Kodak Co. pamphlet *X-Rays*, pp. 36-38.

† Note: The line  $YZ$  should actually occupy a position 6 cm. (in the original) farther away from  $UV$ , but was moved up so as to bring it on to the photographic paper.



of the spectral image considered. The distances  $UY$  and  $VZ$ , representing the incident light intensities corresponding to the transmitted intensities  $UW$  and  $VX$ , respectively, could be determined. Owing to a slight regular variation in the emission of the photometer lamp,  $UY$  and  $VZ$  differed slightly. It could, however, be assumed, with fair accuracy, that points on  $YZ$  gave the incident intensities proper to the corresponding points on the photographic record.

From the three lines  $UV$ ,  $WX$ ,  $YZ$  the densities of the various elements of area of the film could be obtained. Table 2 contains the measurements at the maximum of  $L\alpha_1$  (point  $A$ ) on the photometric curves for film C 207.

Table 2.

Image number	Exposure ( $t$ ) in min.	Log $t$	Incident light intensity (cm.)	Transmitted light intensity (cm.)	Density
4	16	1.204	14.87	0.05	2.473
5	10	1.000	13.90	0.22	1.801
6	7	0.845	14.04	0.32	1.632
7	5	0.699	14.10	0.80	1.246
8	3	0.477	14.46	2.48	0.766
9	2	0.301	14.59	4.07	0.554
10	1	0.000	14.52	6.00	0.384

A graph was drawn (Fig. 4) of  $D$  against  $\log t$ . The relative "photographic" intensity at the maximum of  $L\alpha_2$  (point  $B$ ) to that at the maximum of  $L\alpha_1$  (point  $A$ ) could then be obtained by determining the time  $t'$  which corresponded on the graph to the density at  $B$ , for by the reciprocity law

$$Nt = Nt',$$

where  $t$  is the actual exposure time.

To obtain the true relative intensities, the following considerations had to be taken into account\*. (1) According to definition the general radiation must be excluded in determining the relative intensities. Measurements showed, however, that the density due to general radiation was so small that the corrections to be applied to the relative intensity measurements were negligible. (2) Owing to the differences of absorption in the film for the different lines, the relative numbers of quanta absorbed in the film are not equal to the relative numbers of incident quanta. Calculations showed that the error was of the order of 1 per cent., and since, further, this correction is in the opposite direction to that for variation in sensitivity with wave-length (by Berthold's expression given previously), it was neglected. (3) The lines overlap. For estimation of the correction an  $\alpha_2$  calibration curve was drawn analogous to the  $\alpha_1$  curve, and intensities at various other points were determined from the curve, relative to that at the peak of  $L\alpha_2$ . The assumption was now made that all the lines were symmetrical and of the same shape.

\* Note: The variation with wave-length of the reflective power of the crystal gives rise to no appreciable error with the limited wave-length range and good calcite crystal used. Cf. Davis and Stempel, *Phys. Rev.* 17, 608 (1921); Wagner and Kulenkampff, *Ann. der Phys.* 68, 369 (1922).

Then the intensity at a point  $C$  at the same distance as the  $\alpha_2$  peak from the  $\alpha_1$  peak, but on the opposite side, gave, subject to correction on account of a contribution due to  $\alpha_3$ , the portion of the intensity at the peak of  $L\alpha_2$  due to  $L\alpha_1$ . The intensity at the peak of  $L\alpha_3$  (point  $D$ ) needed no appreciable correction for the overlapping of  $L\alpha_1$ , and the ratio between this intensity and the portion of the intensity at  $C$  due to  $\alpha_3$  could be assumed to be equal to the ratio between the intensity at the peak  $B$  of  $L\alpha_2$  and that at a point  $F$  at a distance from this peak equal to the distance between  $D$  and  $C$ . The intensity at a point  $E$  at the same distance as the  $\alpha_1$  peak from the  $\alpha_2$ , but on the opposite side, gave the portion of the intensity at the peak of  $L\alpha_1$  due to  $L\alpha_2$ .

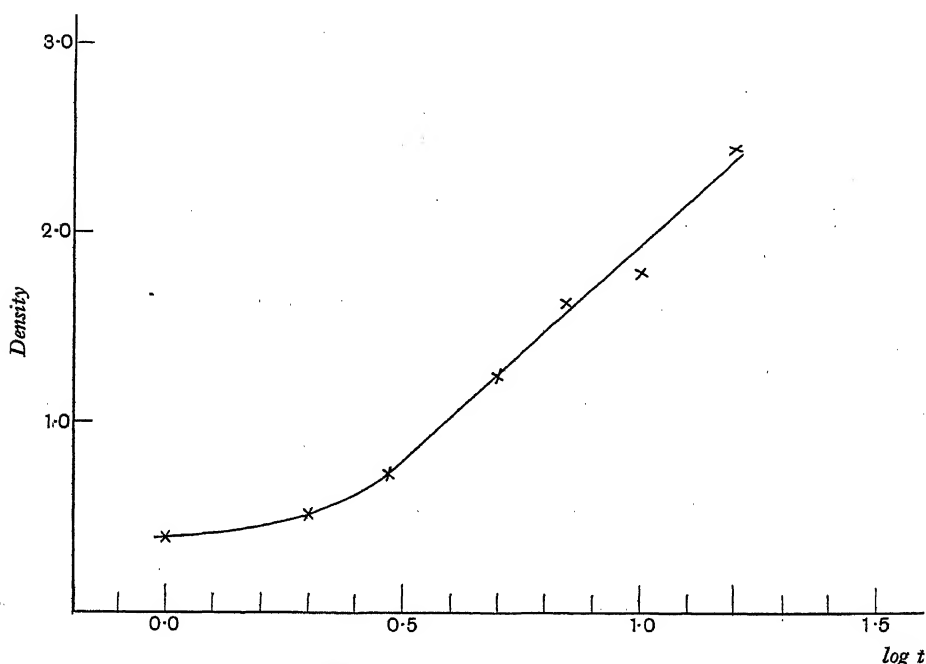


Fig. 4. Density/exposure curve.

The intensities for film G 104 are collected in Table 3:

Table 3.

Intensity at	Spectral image 1	Spectral image 2	Spectral image 3
<i>A</i>	100	100	100
<i>B</i>	17.3	19.0	21.1
<i>C</i>	7.6	8.5	11.2
<i>D</i>	6.9	7.1	7.8
<i>E</i>	2.7	2.9	3.4
<i>F</i>	3.5	3.8	4.5
$L\alpha_3$ at <i>C</i>	1.2	1.5	1.8
$L\alpha_1$ at <i>B</i>	6.4	7.0	9.4
$L\alpha_2$ (corrected)	10.9	12.0	11.7
$L\alpha_1$ (corrected)	97.3	97.1	96.6

## § 4. RESULTS

The intensity ratio for  $La_1 : La_2$  given in Table 4 is in fair accord with the ratio, 100 : 11.1, predicted by Sommerfeld's theory of X-ray line intensities, and thus affords support to the Stoner-Smith theory of electron distribution. The increase of the relative intensity of  $La_3$  with increasing tube voltage is to be expected if  $La_3$  has a higher critical voltage than  $La_{1,2}$ , in accordance with the usually accepted theory of X-ray spark lines\*.

Table 4.

Film no	Tube voltage (R.M.S.)	Relative intensities		
		$La_1$	$La_2$	$La_3$
C 207	—	100	12.0	5.8
G 104	20.0	100	11.8	7.3
G 106	16.2	100	12.2	4.6
Mean		100	12.0	

## § 5. THE RECIPROCITY LAW

The tube voltage was adjusted to about 3000 volts r.m.s., so that the silver  $L$  radiations constituted the majority of the short-wave radiation. The longer wave-length radiations were largely filtered out by an aluminium sheet of thickness sufficient to cut down the silver  $La$  to about one-tenth of its intensity. The slits were removed. Three portions cut from the same film were mounted on attachments to the camera support, and a special shutter was attached in place of the crystal table. Thus by means of the conical bearings the films could be exposed, in turn, at different known distances from the anticathode. Calculations showed that the intensities of radiation falling on the films were to a sufficient approximation inversely proportional to the squares of their distances from the centre of the focal spot. The times of exposure were made inversely proportional to the computed intensities and the measurement of the resultant densities provided a test for the reciprocity law. Results obtained are given in Table 5.

Table 5.

Intensity	Densities	
	Films G 112-4	Films G 115-7
1	1.33 ± 0.02	1.155 ± 0.01
1.74	1.32 ± 0.02	1.155 ± 0.01
7.80	1.31 ± 0.02	1.158 ± 0.01

\* Since the above was written a less accurate measurement of the  $La_1 : L\beta_1$  ratio has been determined. It is 100 : 40. Corrections for absorption etc. (see p. 188) tend to balance out and were within the limits of experimental error, which was 10 per cent.

Thus within the limits of experimental error it is justifiable to assume the validity of the reciprocity law.

In conclusion I wish to express my gratitude to Professor Laby for the continued assistance and encouragement received from him throughout the course of this work. My thanks are also due to Dr L. H. Martin for his helpful advice and interest.

## DISCUSSION

Prof. F. L. HOPWOOD: I should like to congratulate the author on a sound and valuable contribution. I would also point out that although under the conditions under which the author worked it is permissible to use the photographic method for the measurement both of X-ray intensities and of wave-lengths, yet the photographic method for both types of measurement leads to erroneous results in dispersive media. Over what range does the author consider the relation

density  $\propto$  number of quanta absorbed

to be valid, as theoretical considerations would point to another law?

Miss T. J. DILLON asked the author why he had abandoned the tungsten-filament X-ray tube for one with a Wehnelt filament (p. 186 of the paper).

AUTHOR'S reply: The results obtained by Berthold, as shown in the formula on p. 185, throw light on the question raised by Prof. Hopwood. The range over which the assumption that the density varies as the number of quanta is justifiable depends on the accuracy attained in the other parts of the experiment. For the present work it would be of the order of 100 X.U. The expression shows, however, that over a considerably larger range of wave-length the assumption that the density varies as the energy absorbed is justified for moderately long X-radiation.

In reply to Miss Dillon's question, I would say that in the first place it was feared that evaporation from the tungsten filament and deposition of tungsten on the anticathode might lead to errors with the method used. In the second place, the intention was to extend the method for use over a larger range of wave-lengths, in which case the presence of the carbon paper screen (p. 187) would be undesirable.

SPARK SATELLITES OF THE  $L\alpha$  LINES OF SILVER

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*Received December 10, 1928. Read and discussed February 8, 1929*

**ABSTRACT.** The wave-lengths of four spark satellites of silver  $L\alpha$  were measured by a relative method, the results being  $4134\cdot7$ ,  $4130\cdot5$ ,  $4125\cdot6$ ,  $4119\cdot0$  X.U.

IN films taken in connection with the preceding paper, spark satellites were observed on the hard side of the  $L\alpha_1$ . The distances of these lines from  $L\alpha_2$  ( $L\alpha_1$  could not be used, since it had been broadened too much by halation) were measured by the projection method\* usually employed in this laboratory. The mean distances, in terms of divisions of the head of the screw, for three spectral images on film G 104 were as shown in the table.

Spectral image number	$\alpha_2'$	$\alpha_1'$	$\alpha_2''$	$\alpha_1''$
1	162	211	258	314
2	174	213	256	316
3	177	210	252	314
Mean	171	211	255	315

The notation for  $\alpha_1'$  and  $\alpha_1''$  has been copied from that of Thoraeus† and of van der Tuuk‡. These lines are usually denoted by  $\alpha_3$  and  $\alpha_4$  respectively. The distances of the film and the principal slit from the rotation axis of the crystal were each adjusted to  $10\cdot00 \pm 0\cdot02$  cm. The wave-length of silver  $L\alpha_2$  being taken as  $4153\cdot82$  X.U.§, and the grating space of calcite  $3029\cdot04$  X.U., the wave-lengths come out as

$$\alpha_2' \quad 4134\cdot7 \pm 0\cdot4 \text{ X.U.}$$

$$\alpha_1' \quad 4130\cdot5 \pm 0\cdot2 \quad ,,$$

$$\alpha_2'' \quad 4125\cdot6 \pm 0\cdot4 \quad ,,$$

$$\alpha_1'' \quad 4119\cdot0 \pm 0\cdot2 \quad ,,$$

\* Eddy and Turner, *Proc. R. S. A*, 111, 117 (1926).

† Thoraeus, *Phil. Mag.* 2, 1007 (1926).

‡ Van der Tuuk, *Zeits. für Phys.* 41, 326 (1927).

§ Siegbahn, *The Spectroscopy of X-Rays*, p. 118.

Previous values for  $\alpha_1'$  and  $\alpha_1''$  are

$\alpha_1'$	(Siegbahn's laboratory*)	4131.7 X.U.
$\alpha_1''$	(Coster†)	4119.4 „

Careful examination of tables of wave-lengths was made to make sure that none of these lines could have proceeded from other elements present as impurities in the anticathode. The decreasing order of intensities of the lines is  $\alpha_1'$ ,  $\alpha_1''$ ,  $\alpha_2''$ ,  $\alpha_2'$ .

\* Siegbahn, *The Spectroscopy of X-Rays*, p. 118.

† Coster, *Phil. Mag.* 43, 1070 (1922).

# THE CONSTRUCTION AND CALIBRATION OF A SENSITIVE FORM OF PIRANI GAUGE FOR THE MEASUREMENT OF HIGH VACUA

By L. F. STANLEY, A.R.C.S., B.Sc.

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*Received October 30, 1928. Read and discussed February 22, 1929*

**ABSTRACT.** The low-pressure gauge here described consists of a manometer and a compensator of identical construction placed in the opposite arms of a Callendar-Griffiths bridge. Each comprises, essentially, a loop of 10 cm. of platinum wire, 0.001 in. in diameter, together with a compensating loop of 2 cm. of the same wire. The symmetry of the circuit makes errors due to thermo-electric effects very small. Investigations have been carried out to ascertain how the sensitivity of the instrument depends upon (1) the diameter of the gauge; (2) the temperature of the wire; (3) the temperature of the external walls; (4) the nature of the material of the external walls. The gauge follows variations of pressure with considerable rapidity, and its range of measurement is from  $2 \times 10^{-3}$  mm. to  $4 \times 10^{-6}$  mm. approximately.

## § 1. LOW-PRESSURE MEASUREMENT

THIS work was carried out with the view of producing an instrument capable of measuring the lowest pressures. The instrument very commonly used for measuring pressures less than 1 mm. of mercury is the McLeod gauge. This type of gauge has marked defects, one of the chief being that the reading is that of the partial pressures due to gases, and not the total pressure of gases and vapours; the readings, however, are absolute.

There are, besides, a number of types of low-pressure gauge: the type with which this paper deals is usually known as the Pirani gauge.

### *The Pirani gauge*

The Pirani gauge\* makes use of the fact that, at low pressures, the conductivity of a gas is a function of its pressure, and hence the heat dissipated by a suitable source of heat will vary when the pressure is varied. The gauge of Pirani consisted of a tantalum lamp, the wire being heated by an electric current. The resistance

\* Pirani, *Ver. d. Deutsch. Phys. Ges.* 8, 24 (1906).

of the gauge was measured by a Callendar-Griffiths bridge; a similar lamp, which had been exhausted and sealed off at a low pressure, was placed in the other arm of the bridge to compensate for variations in the air temperature.

C. F. Hale\*, and later, N. R. Campbell†, have made improvements upon the gauge of Pirani.

## § 2. METHOD AND APPARATUS

To obtain a sensitive instrument it is first necessary to investigate the conditions which affect its sensitivity, and then to adjust these conditions so as to obtain a maximum sensitivity. Pirani‡ has shown that the method of calibration giving the greatest sensitivity is that of measuring the change of resistance as a function of the change of pressure, the current being kept constant. The sensitivity of the manometer will be increased by conditions that will tend to make the dissipation of heat by conduction through the gas larger, in comparison with the heat lost by direct radiation and by conduction along the supports. To make the latter loss as small as possible, "anchoring" of the wire was avoided by the use of a short loop only of the wire. In the first instance, this loop consisted of 2.5 cm. of 0.001 in. platinum wire. Its ends were soldered with gold to two thicker leads of platinum wire, which were fused into a glass tube and welded to thick copper leads. The tube was fused at its upper end into a wider tube, so that the latter enclosed the fine wire. The leads were insulated by purified asbestos wool. A similar instrument was prepared, and this was used as a compensator.

### *Preparation of the compensator*

The purpose of the compensator was to minimize errors due to any variations in the external conditions, and it was exhausted, sealed off and placed in the arm of the bridge opposite to that occupied by the manometer. To exhaust the compensator its side tube was partly constricted and then connected by means of glass-tubing to a McLeod gauge and to a Gaede mercury rotary pump. A U-tube, a charcoal-pocket and a drying tube containing  $P_2O_5$  were inserted between the compensator and the pump. The connections were all-glass, and the tubing was kept as wide and as short as possible. Two taps were placed between the apparatus and the pump. The compensator was exhausted by the pump and at the same time heated by an electric furnace to about  $275^\circ C.$ ; the wire was heated to a somewhat higher temperature of  $300^\circ C.$  approximately. The heating was maintained and the pumps kept in operation for several days, to out-gas the instrument thoroughly; the temperature of the heater was finally reduced gradually, liquid air was continuously applied to the charcoal-pocket, and the compensator was then sealed off.

\* C. F. Hale, *Trans. Am. Electrochem. Soc.* 20, 243 (1911).

† N. R. Campbell, *Proc. Phys. Soc.* 33, 287 (1921).

‡ Pirani, *loc. cit.*



The manometer was connected to the apparatus in place of the compensator and heated in the same way as the latter with the pumps working. Fig. 1 illustrates the manner in which the apparatus was connected.

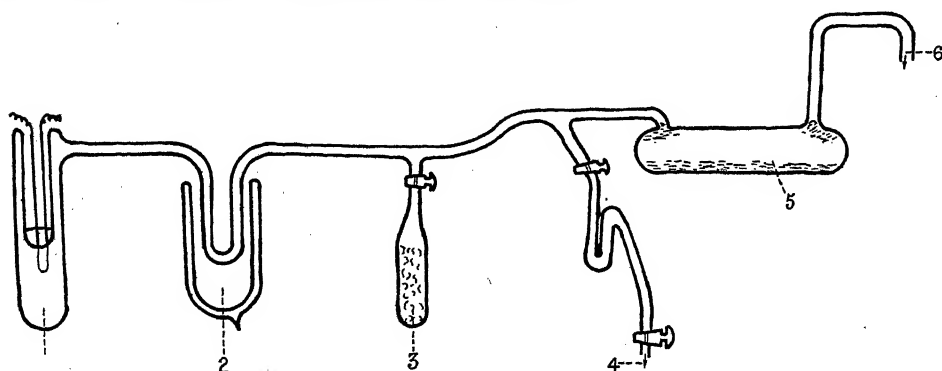


Fig. 1. Construction of apparatus: 1, gauge; 2, liquid air; 3, charcoal-pocket; 4, pump attachment; 5,  $P_2O_5$  tube; 6, McLeod gauge attachment.

### *The electrical connections*

The manometer and compensator were placed in the opposite arms of a Callendar-Griffiths bridge, the connections being made through mercury cups. The

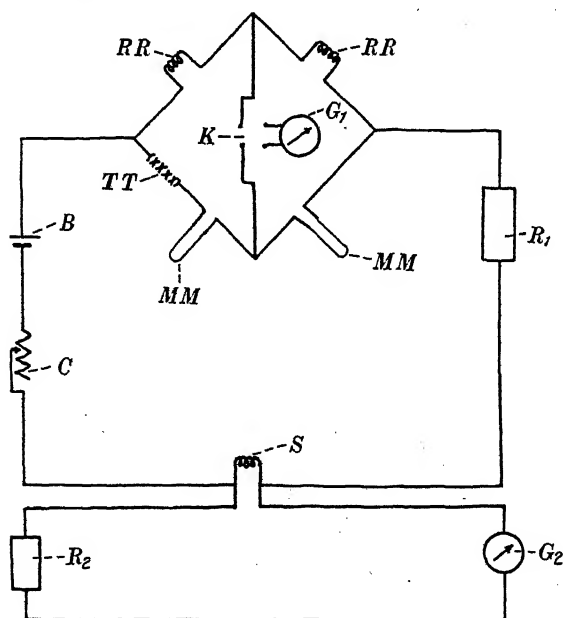


Fig. 2. Electrical connections.

arrangement of the electrical circuit is represented in Fig. 2.  $RR$  are the ratio arms of the bridge,  $TT$  the bridge-coils,  $MM$  the manometer and compensator,  $G_1$  a galvanometer for indicating the point of balance on the bridge, and  $B$  a two-volt

accumulator connected in series with a carbon rheostat  $C$ , a  $0.1$  ohm resistance  $S$ , and a resistance box  $R_1$  containing multiples and sub-multiples of the ohm. In parallel with  $S$  are connected a resistance box  $R_2$  and a moving coil galvanometer  $G_2$  of high sensitivity. The current was kept constant by the carbon rheostat  $C$ , a very sensitive control being obtained when the carbons were tightly packed. The galvanometer  $G_2$  served to indicate the constancy of the current.

### § 3. EXPERIMENTAL INVESTIGATION OF THE SENSITIVITY OF THE INSTRUMENT

Experiments were carried out in order to determine in what manner the sensitivity of the gauge was affected by:

1. The diameter of the gauge.
2. The temperature of the exterior walls of the manometer.
3. The temperature of the loop itself.
4. The nature of the material of the external walls.

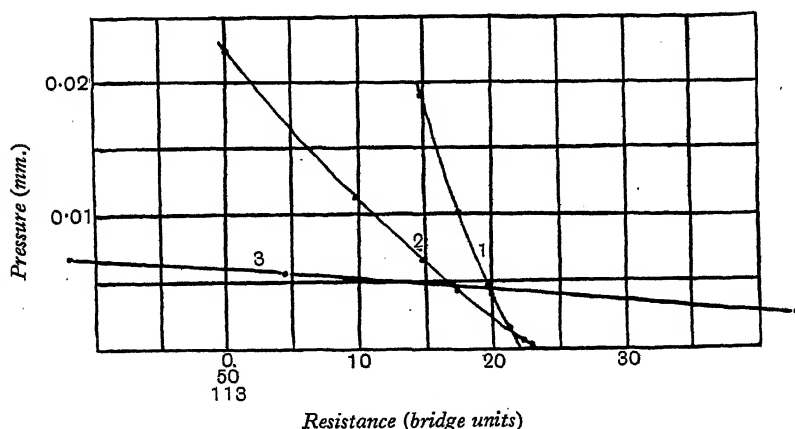


Fig. 3. Resistance-pressure curves for glass gauge No. 1, with external walls at the temperatures of (1) steam, (2) melting ice, (3) liquid air.

To investigate the first condition two sets of instruments were made, the first being  $2.7$  cm. in diameter and the second  $1.7$  cm. When readings were being taken the manometer and the compensator were immersed in melting ice, the loops were heated by a constant current sufficient to raise their temperatures to  $90^{\circ}$  C. at the lowest pressures, and the U-tube was immersed in liquid air in order to free the manometer from the presence of mercury vapour. The system was exhausted to about  $0.01$  mm., the taps were turned, and the point of balance was determined on the bridge, the pressure being simultaneously determined as accurately as possible by the McLeod gauge. In this way a series of readings of the bridge resistance and the corresponding pressure down to the lowest pressures were obtained. The pressures were plotted as ordinates against the corresponding

readings of the bridge as abscissae. The curves obtained indicated that, at low pressures, the diameter of the tubes, when of the order mentioned above, has no effect on the sensitivity of the instrument. One might expect this from the fact that, at pressures below 0.001 mm., the mean free path of most gases is greater than 10 cm.

The chief factor controlling the sensitivity of the gauge is, undoubtedly, the second one, namely, the temperature of the external walls of the gauge. This fact is indicated by Fig. 3, in which are plotted graphs of pressure against bridge resistance, the exterior walls of the manometer and compensator being at the temperatures of (1) steam, (2) melting ice, and (3) liquid air. These graphs show clearly that the lower the external temperature of the manometer and compensator, the more sensitive is the instrument to variations of pressure. This is the result of the fact that, when the pressure is lowered, the change in the rate of dissipation of heat will be the greater, the lower the temperature of the walls of the manometer.

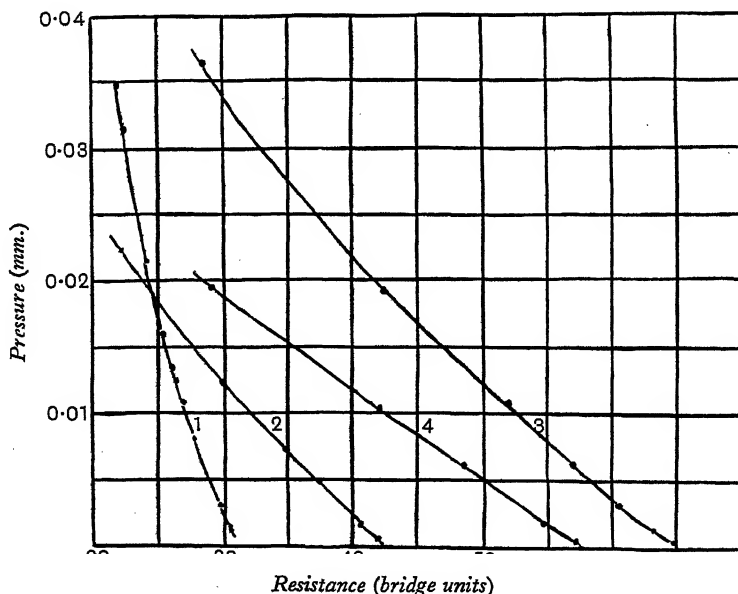


Fig. 4. Resistance-pressure curves for glass gauge No. 1, with wire at temperatures (1) 30° C., (2) 100° C., (3) 130° C., (4) 160° C.

Fig. 4 illustrates the manner in which the third condition, namely, the temperature of the wire, affects the sensitivity of the gauge. There are four graphs, the temperatures of the filament being 30, 100, 130 and 160° C. respectively. The less the slope of the graph, the greater the sensitivity of the gauge. Little increase in sensitivity is obtained by heating the wire above 100° C., as is shown in Table I, whereas an increase in possible sources of error, such as those due to fluctuations in the heat loss along the leads, is likely to occur at such temperatures.

Table 1. Relation between sensitivity and temperature of filament

Temperature °C.	Slope of graphs, Fig. 4 (mm. per cm. of bridge wire)
30	0.0017
100	0.0009
130	0.0007
160	0.0006

*Effect of metal walls on the sensitivity of the instrument*

In order to ascertain the manner in which the thermal conductivity of the external walls might affect the sensitivity of the instrument, a gauge having its walls of metal instead of glass was constructed. A solid rod of brass was turned into the form of a hollow cylinder and flanged at the top. A glass manometer, similar to one of those already calibrated, was constructed with the exception of the lower half of the external tube; the brass cylinder was turned to take the place of the latter, and a sealing-wax joint was made, the flange serving to ensure that the joint was air-tight.

The instrument was calibrated, the temperature of the filament being raised to 55° C. approximately. The graph (B), Fig. 7, indicates that the instrument was but slightly more sensitive than the glass one. Such a metal instrument, however, gave rise to great difficulty owing to the continuous evolution of gas from its walls and the impossibility of keeping the compensator sealed off at a low pressure. The sensitivity of the metal gauge was deemed insufficient to warrant the construction of a gauge of gas-free metal.

#### § 4. MODIFICATION OF THE INITIAL FORM OF THE GAUGE

As the resistance of the form of the gauge already described changed by a small value only when the pressure was reduced to the lowest values, the gauge was modified by increasing the length of the loop to 10 cm. A loop longer than this would not be convenient unless anchored in some way. To minimize still further the errors due to fluctuations in heat loss along the leads, duplicate pairs of leads were inserted in the compensator and the manometer, and each pair was connected by 2 cm. of wire cut from the same reel as the longer loops. The short loop of the manometer was placed in the arm of the bridge containing the longer loop of the compensator, and *vice versa*. The presence of thermo-electric effects cannot, in this case, be eliminated by reversing the current through the resistance to be measured, as the point of balance would thereby be lost. The method adopted, therefore, was to obtain symmetry in the bridge circuit by adjusting the resistances of the manometer and compensator to equality within 0.1 per cent. This was

effected first by adjusting the length of the wire and finally by stretching the wire. The manometer is illustrated in Fig. 5.

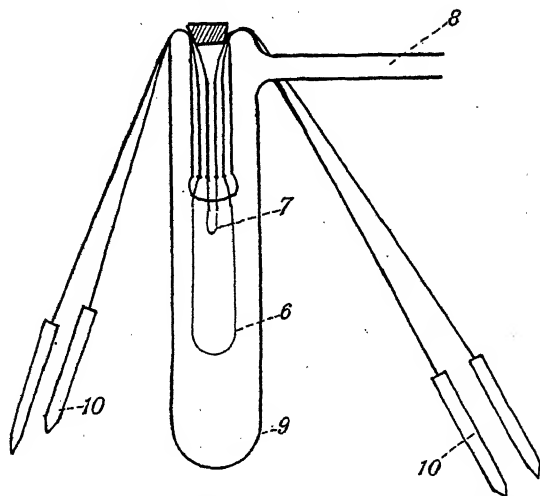


Fig. 5. Construction of modified form of gauge. 6, loop of 10 cm. of 0.001 in. platinum wire; 7, compensating loop of 2 cm. of identical wire; 8, tube for connection to pressure system; 9, glass tube 2.7 cm. diameter; 10, leads for connection to bridge.

### *The calibration*

The compensator was connected to the system previously described and sealed off at a pressure of 0.00018 mm. in the manner indicated. The manometer was then fused in place of the compensator and out-gassed. To maintain the external temperature of the walls as constant as possible, the gauge was immersed in a tank containing ice and water which could be thoroughly stirred, a constant stream of ice-cold water being sent past the gauge.

In the first calibration the filament was heated, at the lowest pressures, to a temperature of 23° C. only, by a constant current of 0.008835 amp. in the main circuit. Fig. 6 gives the calibration curve. The slope of the graph at the lowest pressures indicates that 1 mm. shift along the bridge wire corresponds to a change of pressure of  $8 \times 10^{-6}$  mm.

### § 5. NOTE ON THE ACCURACY OF THE ORDINARY TYPE OF McLEOD GAUGE

In Fig. 6 curve (b) is similar to curve (a), identical readings being plotted on a magnified scale; in (b) all the readings do not lie on the calibration curve, and this fact was attributed primarily to inaccuracies in the reading of the McLeod gauge. On the assumption that the calibration curve (b) was correct, the mean error in the readings of the pressure taken with this McLeod gauge between  $10^{-3}$  mm. and  $10^{-4}$  mm. was 4.5 per cent.

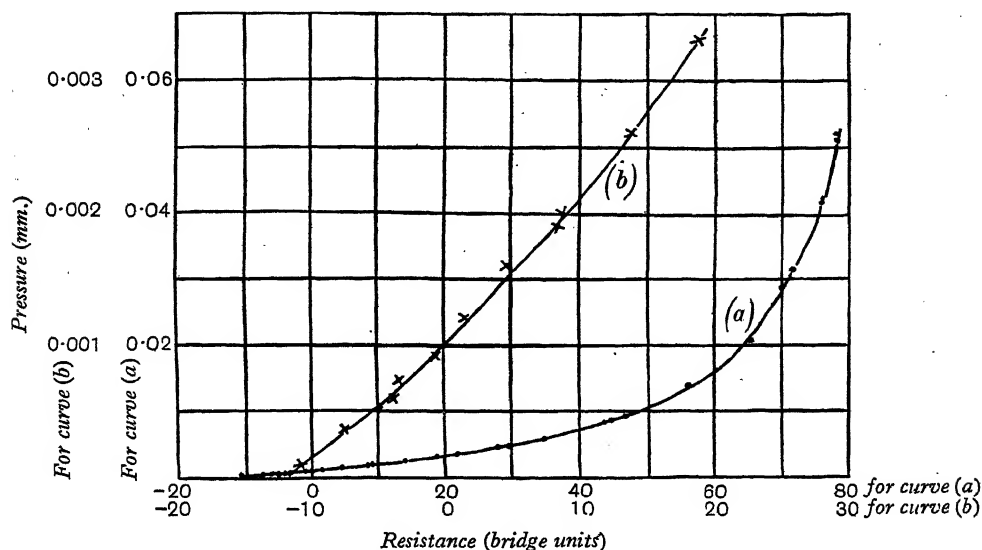


Fig. 6. Pressure-resistance curves for glass gauge No. 2.

### The Dunoyer-McLeod gauge

A design of McLeod gauge due to M. Dunoyer was acquired with the view of making a more accurate calibration. This gauge is, in effect, a compound form of the original type, and proved very satisfactory for the measurement of low pressures. With this gauge the Pirani gauge was re-calibrated. The current through the main circuit was kept constant at 0.01591 amp., the temperature of the wire being thereby raised to 55° C. at the lowest pressures. The readings plotted were obtained over a course of a week or two, and they all fall very closely on the calibration curve (A), Fig. 7.

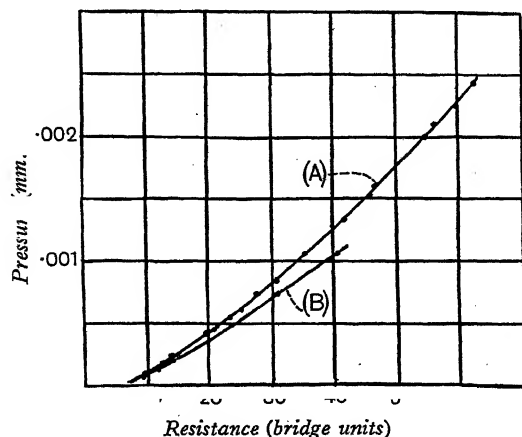


Fig. 7. Pressure-resistance curves for (A) glass gauge No. 2, and (B) metal gauge.

Provided the pressure in the system was steady, readings could be repeated to agree to 1 mm.; it was found that the change of pressure corresponding to 1 mm. shift along the bridge wire was, at the lowest pressures,  $3.4 \times 10^{-6}$  mm. The instrument is, therefore, suitable for measuring changes of pressure of this order at low pressures. Figs. 6 and 7 indicate that even at the lowest pressures "a straight-line law" of the variation of pressure with resistance does not appear to be followed accurately, under the relevant conditions of the measurement of pressure and of resistance. The change of the slope of the graph, however, for pressures less than  $5 \times 10^{-4}$  mm. is very small.

#### § 6. CONCLUSIONS

The low-pressure gauge described can be constructed fairly easily, and it will follow moderately rapid variations of pressure; the limit to the speed of measurement is governed by the time necessary to obtain a point of balance on the bridge wire.

The instrument is capable of measuring pressures within the range between  $2 \times 10^{-3}$  mm. and  $4 \times 10^{-6}$  mm. It is not particularly suitable for rough-and-ready measurements of pressure, as a certain amount of care is required in its use. It might, however, be useful when the value of the pressure needs to be known as accurately as possible, as is the case in some scientific researches.

In conclusion, I have to thank Miss M. Bell, B.Sc., D.I.C., for useful advice on the production of high vacua, and also Professor H. L. Callendar, F.R.S., for advice on the method of procedure.

#### DISCUSSION

Miss T. J. DILLON: Would the author kindly say (1) what gas was introduced into the tube to produce the increase of pressure; (2) what method was used for finding the temperature of the filament; (3) whether the sensitivity of the gauge was studied at any high temperatures?

Mr L. C. JESTY: I should like to ask the author his reasons for baking his comparison gauge for several days at such a low temperature as  $275^{\circ}$ . Soft glass bulbs will stand a temperature of  $400^{\circ}$ – $450^{\circ}$  when evacuated, and therefore I consider that baking for an hour or even less at  $400^{\circ}$  would have degassed the glass more efficiently.

Prof. C. H. LEES: It would be of interest if Mr Stanley would say what influence the size of the vessel containing the filament has on the constant of the instrument.

AUTHOR'S reply: The gas used in the calibration of the instrument was dry air, freed from  $\text{CO}_2$ . To measure the temperature of the filament the gauge was used as a platinum thermometer, its fundamental interval being determined by finding its resistance at  $0^{\circ}$  C. and at  $100^{\circ}$  C. The comparative instability of the gauge,

together with the fact that at high temperatures a considerable amount of the heat is lost by radiation at a rate independent of the pressure, were the reasons why the filament was not raised to higher temperatures.

It has been shown that soda glass evolves gas in two well-defined stages, one below 300° C., the other above this temperature\*. It is concluded that the products removed below 300° C. are adsorbed gases, while at higher temperatures there is an actual decomposition of the glass itself. As the walls of the gauge do not experience temperatures above room temperature, it is sufficient to remove the adsorbed gases only.

The sensitivity of the gauge is independent of the diameter of the instrument at low pressures, provided that the diameter be less than the mean free path of the molecules. At pressures below 0.001 mm., the mean free path in most gases is greater than 10 cm.

\* R. G. Sherwood and J. E. Shrader, *Journ. Am. Chem. Soc.* **40** (1918).



# THE FREE PERIODS OF A COMPOSITE ELASTIC COLUMN OR COMPOSITE STRETCHED WIRE

By CHARLES H. LEES, D.Sc., F.R.S.

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**ABSTRACT.** The free periods of the longitudinal oscillations of an elastic column, one portion of which has different elastic properties from the remainder, are determined for different positions of the junction when both ends of the column are nodes, when one is an antinode, and when both are antinodes. A graphical method of dealing with the problems is developed. Observations in the case of a composite stretched wire agree with the theoretical results.

## § 1. INTRODUCTION

SOME investigations which are being carried out at the Safety in Mines Research Stations at Sheffield and at Buxton have rendered it desirable that the possible oscillations of a column of gas, one portion of which is at a temperature  $T_1$  and the other at a temperature  $T_2$ , should be investigated in the three possible cases, i.e. when the column is closed at each end, when one end is open and when both ends are open to the atmosphere.

For displacements which are not too large, the problem of the longitudinal oscillations of an elastic column of a single material and that of the transverse oscillations of a thin stretched wire of a single material lead to the same differential equation, and the end conditions for a column of gas closed at each end or of a rod clamped at each end are identical with those for a wire stretched between fixed supports.

The problem of the reflection which a sudden change of linear density produces in the case of a progressive wave travelling along a composite stretched wire has been considered by Rayleigh\*, but the case of standing waves does not appear to have been treated. In the case of a composite column of gas or a composite stretched wire the change is generally in the mass per unit length only, the adiabatic elasticity in the case of the gas and the stretching force in the case of the wire remaining constant. The free periods of a given length of composite column or wire then lie between those of the same length when composed entirely of one or other of the two constituent gases or wires. But the effect on the periods of a small change of position of the junction of the two constituents is small when the junction is near a node, since the motion there is small, and large when it is near an antinode where the motion is large. The relation between the frequency and the position of the junction cannot therefore be a linear one.

When the composite column consists of two gases with different values of  $\gamma$ , the ratio of the specific heats at constant pressure and at constant volume, or of

\* *Sound*, Vol. 1, Section 148 a (1896).

two liquids or solids with different adiabatic elasticities, the relation between the frequency and position of the junction is less simple and the frequency may not in all cases lie between those of the same length of the constituents.

## § 2. BOTH ENDS NODES

To deal with the general case, in which at the junction of the two constituents changes of both elasticity and density may occur, take the  $x$  axis along the axis of the column, let  $x$  be the undisplaced position of a point and  $\xi$  its displacement forward along the  $x$  axis in the case of longitudinal oscillations, or at right angles to the  $x$  axis in the case of transverse oscillations, at the time  $t$ .

Then the equation  $\partial^2 \xi_1 / \partial t^2 = (F_1/m_1) \partial^2 \xi_1 / \partial x^2$

holds for each point of the first constituent and the equation

$$\partial^2 \xi_2 / \partial t^2 = (F_2/m_2) \partial^2 \xi_2 / \partial x^2 \quad \dots\dots(2.1)$$

for each point of the second, where  $F_1, F_2$  are the moduli of adiabatic elasticity for the longitudinal displacements in the column or the stretching force in the wire, and  $m_1, m_2$  the masses per unit volume in the column or per unit length in the wire\*.

The solutions of these equations are

$$\xi_1 = a_1 \sin \{2\pi n x / \sqrt{(F_1/m_1)}\} \cos 2\pi n t$$

and

$$\xi_2 = a_2 \sin \{2\pi n (L - x) / \sqrt{(F_2/m_2)}\} \cos 2\pi n t \quad \dots\dots(2.2),$$

where the time is reckoned from the instant when the displacements have their maximum values,  $L$  is the total length of the column or wire,  $n$  the frequency of the oscillation and  $a_1$  and  $a_2$  are constants.

If  $n_1$  be the fundamental frequency when the whole length is occupied by the first constituent and  $n_2$  when by the second, we have

$$2\pi n_1 L / \sqrt{(F_1/m_1)} = \pi \text{ and } 2\pi n_2 L / \sqrt{(F_2/m_2)} = \pi.$$

Hence the equations may be written

$$\xi_1 = a_1 \sin (\pi n x / n_1 L) \cos 2\pi n t$$

and

$$\xi_2 = a_2 \sin [\pi n (L - x) / n_2 L] \cos 2\pi n t \quad \dots\dots(2.3).$$

If  $l_1$  be the distance of the junction of the two constituents from the origin, we must have at  $x = l_1$  the displacements identical and the forces transmitted through the junction identical. That is at  $x = l_1$ ,  $\xi_1 = \xi_2$  and  $F_1 (\partial \xi_1 / \partial x) = F_2 (\partial \xi_2 / \partial x)$ .

Hence  $a_1 \sin (\pi n l_1 / n_1 L) = a_2 \sin \{\pi n (L - l_1) / n_2 L\}$

and  $F_1 (a_1 / n_1) \cos (\pi n l_1 / n_1 L) = -F_2 (a_2 / n_2) \cos \{\pi n (L - l_1) / n_2 L\}$ .

Thus the frequency  $n$  is subject to the condition

$$(n_1 / F_1) \tan (\pi n l_1 / n_1 L) = - (n_2 / F_2) \tan \{\pi n (L - l_1) / n_2 L\} \quad \dots\dots(2.4).$$

Let  $n l_1 = n_1 L p_1$  and  $n (L - l_1) = n_2 L p_2$ , where  $p_1$  and  $p_2$  are constants. The equation becomes

$$(n_1 / F_1) \tan p_1 \pi = - (n_2 / F_2) \tan p_2 \pi \quad \dots\dots(2.5).$$

\* Rayleigh, *Sound*, Vol. 1, Sections 122 and 152; Vol. 2, Section 249 (1896).

For any assigned value of  $p_1$  this equation allows the corresponding value of  $p_2$  to be calculated; then the equation

$$n = p_1 n_1 + p_2 n_2 \quad \dots\dots(2.6)$$

gives the frequency  $n$ , and

$$l_1/L = p_1 n_1/n \quad \dots\dots(2.7)$$

the position  $l_1$  of the junction of the two constituents. The series of possible angles for the same value of the tangent gives the frequencies of the fundamental and of the harmonics. It is therefore only necessary to calculate  $p_2$  for a few assigned values of  $p_1$  between 0 and 1, to allow the curve connecting the frequency with the position of the junction to be drawn for both fundamental and harmonics.

For the fundamental, while  $p_1$  varies from 0 to 0.5 and to 1,  $p_2$  varies from 1 to 0.5 and 0, giving at these values  $n = n_1, (n_1 + n_2)/2$  and  $n_2$  respectively, and  $l_1/L = 0, n_1/(n_1 + n_2)$  and 1 respectively.

For the first harmonic, while  $p_1$  varies from 0 to 0.5, 1.0, 1.5 and 2,  $p_2$  varies from 2 to 1.5, 1.0, 0.5 and 0, giving at these values  $n = 2n_2, 0.5n_1 + 1.5n_2, n_1 + n_2, 1.5n_1 + 0.5n_2$  and  $2n_1$  respectively, and  $l_1/L = 0, n_1/(n_1 + 3n_2), n_1/(n_1 + n_2), 3n_1/(3n_1 + n_2)$  and 1.0 respectively.

For the second harmonic  $p_1$  varies from 0 to 3 and  $p_2$  from 3 to 0 with corresponding values for  $n$  and  $l_1/L$ .

If  $x$  is at a node in the first constituent, equation (2.3) shows that

$$x/L = \text{integral multiple of } n_1/n,$$

and if it is at an antinode

$$x/L = \text{half an odd integral multiple of } n_1/n.$$

If it is at a node in the second

$$(L - x)/L = \text{integral multiple of } n_2/n,$$

and if at an antinode

$$(L - x)/L = \text{half an odd integral multiple of } n_2/n \quad \dots\dots(2.8).$$

The junction itself is therefore a node if  $p_1$  in  $l_1/L = p_1 n_1/n$  is an integer, and is an antinode if  $p_1$  is half an odd integer .....(2.9).

### § 3. VARIATION OF FREQUENCY

To determine whether the frequency reaches a maximum or minimum for any position of the junction we differentiate the equation for  $n$ , (2.6), and the equation for  $p_1$  and  $p_2$ , (2.5), and on eliminating  $dp_1$  and  $dp_2$  we get

$$(n_2 \cdot n_1/F_1) \sec^2 p_1 \pi = (n_1 \cdot n_2/F_2) \sec^2 p_2 \pi$$

or

$$F_1 \cos^2 p_1 \pi = F_2 \cos^2 p_2 \pi$$

as the condition for the frequency to be a maximum or a minimum. Substituting tangents and eliminating  $\tan p_2$ , by help of equation (2.5) we get

$$\tan^2 p_1 \pi = \{(F_1/F_2)^2 - (F_1/F_2)\} / \{(F_1/F_2) - (n_1/n_2)^2\} = \{(F_1/F_2) - 1\} / \{1 - (m_2/m_1)\}$$

$$\text{and} \quad \tan^2 p_2 \pi = \{1 - (F_2/F_1)\} / \{(m_1/m_2) - 1\} \quad \dots\dots(3.1),$$

which determine  $p_1$  and  $p_2$  and hence  $l_1$  for a maximum or minimum  $n$ .

Hence, for the frequency to have a maximum or a minimum,  $F_1/F_2$  must lie between 1 and  $(n_1 F_2/n_2 F_1)^2$  or 1 must lie between  $F_1/F_2$  and  $m_2/m_1$ .

If  $F_1$  be equal to  $F_2$ , as it will if we are dealing with a composite stretched wire or a column of gas at constant pressure with  $\gamma$  the same for each constituent, or with any column in which each constituent has the same adiabatic elasticity,  $\tan^2 p_1 \pi = 0$  and for the maximum  $n$  of the fundamental the junction lies at one end, for the minimum at the other end of the wire.

#### § 4. GRAPHICAL SOLUTION

The required solutions of the conditional equation (2.5) may be obtained and the relations between the quantities which enter into the problem readily seen from the following graphical construction.

From the point  $A$  of a horizontal line mark off in opposite directions  $AC_1$  and  $AC_2$  equal on some convenient scale to the fundamental frequencies  $n_1$  and  $n_2$

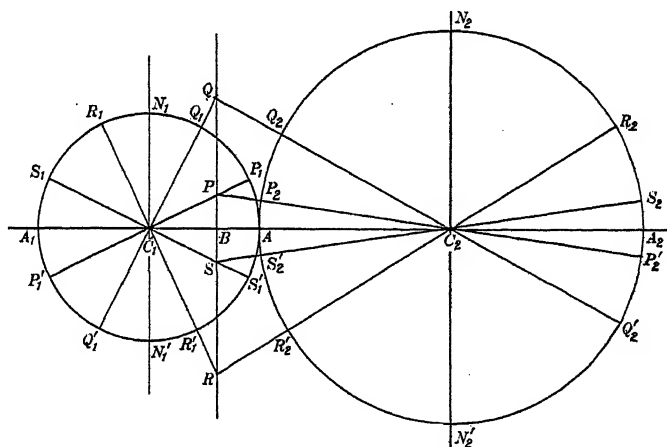


Fig. 1.  $P_1C_1A = p_1\pi$ ,  $P_2C_2A_2 = p_2\pi$ ,  $n\pi = AP_1 + A_2P_2$ ,  $l_1/L = AP_1/(AP_1 + A_2P_2)$ .

respectively, and with centres  $C_1$  and  $C_2$  and radii  $C_1A$ ,  $C_2A$  respectively, describe two circles cutting the horizontal in  $A_1$  and  $A_2$ ; these circles we may call "the  $n_1$  and  $n_2$  circles." Find the position of the point  $B$  such that  $C_1B : BC_2 :: n_1/F_1 : n_2/F_2$  and through  $B$  draw the vertical  $BPQ$ . Join  $P$  to  $C_1$  and  $C_2$  and produce each if necessary to cut the circumference of the  $n_1$  circle in  $P_1$ ,  $P_1'$  and the  $n_2$  circle in  $P_2P_2'$ ,  $P_1$  and  $P_2$  being the points nearest to  $A$  at which the circles are cut. Then  $P_1C_1A$  and  $P_2C_2A_2$  are the principal values of the angles  $p_1\pi$  and  $p_2\pi$  of the conditional equation (2.5), and other values are obtained by adding integral multiples of  $\pi$  to the principal values. The arc  $AP_1$  of the  $n_1$  circle is  $n_1p_1\pi$  and the arc  $A_2P_2$  of the  $n_2$  circle is  $n_2p_2\pi$ . Hence  $n\pi = (\text{arc } AP_1 + \text{arc } A_2P_2)$  and the position of the junction is given by  $l_1/L = \text{arc } AP_1/(\text{arc } AP_1 + \text{arc } A_2P_2)$ . As  $P$  moves along

$BPQ$  to  $Q$  we get the arcs  $AQ_1$ ,  $A_2Q_2$  etc. and when it reaches  $+\infty$  the arcs  $AN_1$  and  $A_2N_2$  subtend angles of  $\pi/2$  at  $C_1$  and  $C_2$ . Hence the corresponding frequency  $n$  is the mean of  $n_1$  and  $n_2$ , and the junction is at a point  $l_1$  such that  $l_1/L = n_1/(n_1 + n_2)$ . The point  $P$  now moves to  $-\infty$  and approaches  $B$  from below. If  $R$  be one of its positions the arcs are now  $AR_1$  and  $A_2R_2$ , which as  $R$  approaches  $B$  become  $\pi$  and  $0$  respectively.

For the positions of the nodes and antinodes for any values of  $p_1$  and  $p_2$  which satisfy (2.5) we use the relations (2.8).

The relations (2.9) show that for the fundamental the junction is an antinode for  $p_1 = 0.5$  and therefore for  $l_1/L = n_1/(n_1 + n_2)$ , and for the first harmonic the junction is an antinode for  $p_1 = 0.5$  and  $1.5$  and therefore for  $l_1/L = n_1/(n_1 + 3n_2)$  and  $3n_1/(3n_1 + n_2)$ , and a node for  $p_1 = 1.0$  and therefore for  $l_1/L = n_1/(n_1 + n_2)$ .

Fig. 1 has been drawn to illustrate the case in which  $n$  for the fundamental has a maximum value greater than  $n_2$ , the higher of the two constituent frequencies, and a minimum less than  $n_1$ , the lower, and corresponding maxima and minima for the harmonics.

If  $B$  in the figure coincide with  $A$  the maximum for the fundamental is at  $n_2$  and the minimum at  $n_1$ , the rates of change of  $n$  being zero at these points.

If  $B$  move to the other side of  $A$  there are no maxima or minima, the condition of section 3 being no longer satisfied.

## § 5. EXPERIMENTS ON WIRES

In order to verify the above theory experimentally, two steel wires of diameters  $0.021$  and  $0.041$  cm. respectively and about a metre long were attached to each other by silver solder and stretched about  $3$  cm. above the bench by a weight of  $1.5$  kg. hanging over a pulley. Underneath the wire two knife-edge supports  $50$  cm. apart, attached to a lath, could be placed so that the joint came in any required position between the knife edges. Two additional knife-edge supports were placed one on each side of the former two, and were so adjusted that the three lengths of wire between the four knife edges were in unison. This result was secured by gently plucking one of the side lengths and seeing that the centre and other side lengths were both set into vibration. The resonance was only considered satisfactory when either side length when plucked would set the other lengths into vibration. The side lengths and the distance of the junction from one knife edge were then measured. From the side lengths the frequency was calculated, the lengths to give a frequency of  $256$  having been found previously to be for the thick wire  $25.7$  cm., and for the thin  $49.7$  cm. It was found advantageous to place a light knife edge on the top of the wire at the point where it passed over each lower knife edge.

The curves of Fig. 2 show the relation found between the position of the joint and the frequency of the vibration. The observed\* values agree very closely with the calculated ones.

\* I have to thank Mr D. J. Fewings, one of my senior students, for taking these observations.

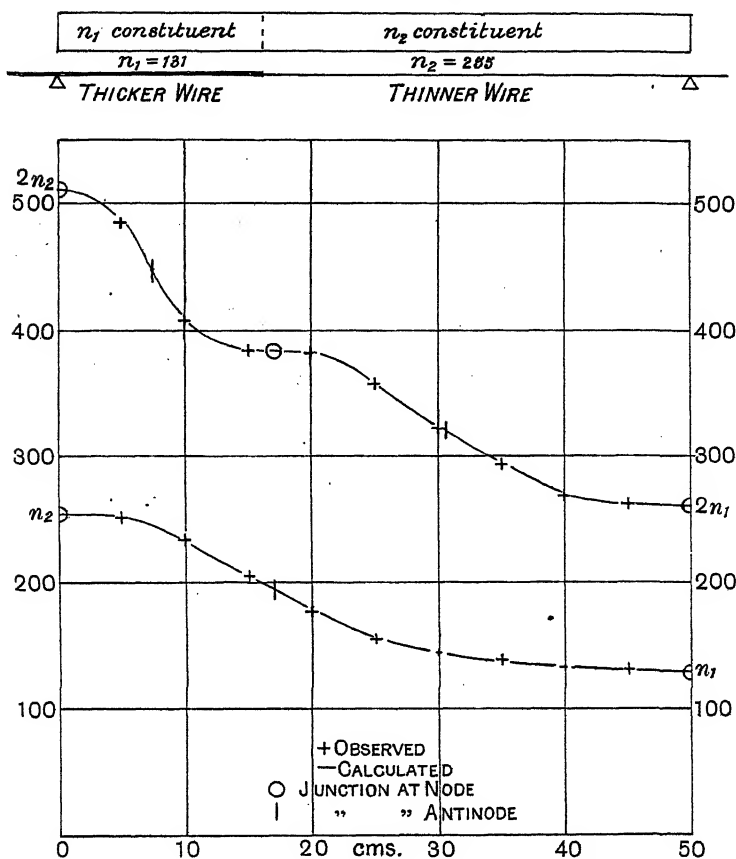


Fig. 2. Frequencies of composite column, with a node at each end, for different positions of junction.

Table 1, which has been calculated for the two wires, shows how readily the solutions of the conditional equation (2.5) may be written down after the first pair of values of  $p_1$  and  $p_2$  have been calculated.

#### § 6. ONE END AN ANTINODE

When one end only of the column is a node the other an antinode, as in a resonance tube closed at the bottom and containing a gas denser than air\* in its lower part, the solutions of the differential equations of § 2 become

$$\xi_1 = a_1 \sin \{2\pi n x / \sqrt{(F_1/m_1)}\} \cos 2\pi n t$$

and

$$\xi_2 = a_2 \cos \{2\pi n (L - x) / \sqrt{(F_2/m_2)}\} \cos 2\pi n t \quad \dots\dots(6.1),$$

$L$  being the length of the column, or in the case of a gas column the length plus the correction for the open end which is approximately 0.3 times the diameter of the column.

\* So long as the open end of the tube is an antinode the gas in the upper part of the tube need not be air.

If  $n_1$  is the frequency of vibration of the column when composed entirely of the first constituent and  $n_2$  when composed entirely of the second constituent we have

$$2\pi n_1 (L/\sqrt{F_1/m_1}) = \pi/2 \text{ and } 2\pi n_2 (L/\sqrt{F_2/m_2}) = \pi/2.$$

Hence the equations for the displacements may be written

$$\xi_1 = a_1 \sin \{(\pi/2) nx/n_1 L\} \cos 2\pi nt$$

and

$$\xi_2 = a_2 \cos [(\pi/2) n (L - x)/n_2 L] \cos 2\pi nt \quad \dots\dots(6.2).$$

Table 1. Composite wire of Fig. 2

Case for which  $n_1 = 131$ ,  $n_2 = 255$ ,  $\tan p_2\pi = -(n_1/n_2)$ ,  $\tan p_1\pi = -0.514 \tan p_2\pi$ .

$p_1$	$p_1\pi$	$\tan p_1\pi$	$\tan p_2\pi$	$p_2\pi$	$p_2$	$p_1 n_1$	$p_2 n_2$	$n$	$l_1/L$
Fundamental, $p_1$ and $p_2$ between 0 and 1									
0.0	0°	0.0	0.0	180.0°	1.0	0	255	255	0.0
0.2	36	0.727	-0.374	159.5	0.886	26	226	252	0.103
0.4	72	3.078	-1.582	122.3	0.679	52	173	225	0.231
0.5	90	$\infty$	$\infty$	90.0	0.500	66	127	193	0.339
0.6	108	-3.078	1.582	57.7	0.321	79	82	161	0.491
0.8	144	-0.727	0.374	20.5	0.114	105	29	134	0.784
1.0	180	0.0	0.0	0.0	0.0	131	0	131	1.0
First harmonic, $p_1$ and $p_2$ between 0 and 2									
0.0	0°	0.0	0.0	360.0°	2.0	0	510	510	0.0
0.2	36	0.727	-0.374	330.5	1.886	26	481	507	0.051
0.4	72	3.078	-1.582	302.3	1.679	52	428	480	0.108
0.5	90	$\infty$	$\infty$	270.1	1.500	66	382	448	0.147
0.6	108	-3.078	1.582	237.7	1.321	79	337	416	0.190
0.8	144	-0.727	0.374	200.5	1.114	105	284	389	0.270
1.0	180	0.0	0.0	180.0	1.0	131	255	386	0.339
1.2	216	0.727	-0.374	159.5	0.886	157	226	383	0.410
1.4	252	3.078	-1.582	122.3	0.679	183	173	356	0.514
1.5	270	$\infty$	$\infty$	90.0	0.500	197	127	324	0.606
1.6	288	-3.078	1.582	57.7	0.321	210	82	292	0.719
1.8	324	-0.727	0.374	20.5	0.114	236	29	265	0.891
2.0	360	0.0	0.0	0.0	0.0	262	0	262	1.0

At the junction of the two constituents,  $x = l_1$ , we have as before

$$\xi_1 = \xi_2 \text{ and } F_1 (\partial \xi_1 / \partial x) = F_2 (\partial \xi_2 / \partial x).$$

Hence

$$a_1 \sin \{(\pi/2) nl_1/n_1 L\} = a_2 \cos \{(\pi/2) n (L - l_1)/n_2 L\}$$

and

$$F_1 (a_1/n_1) \cos \{(\pi/2) nl_1/n_1 L\} = F_2 (a_2/n_2) \sin \{(\pi/2) n (L - l_1)/n_2 L\}.$$

Thus the frequency  $n$  satisfies the condition

$$(n_1/F_1) \tan \{(\pi/2) nl_1/n_1 L\} = (n_2/F_2) \cot \{(\pi/2) n (L - l_1)/n_2 L\}.$$

Writing again  $nl_1 = n_1 L p_1$ ,  $n (L - l_1) = n_2 L p_2$ , where  $p_1$  and  $p_2$  are constants, the condition becomes

$$(n_1/F_1) \tan (p_1 \pi/2) = (n_2/F_2) \cot (p_2 \pi/2) = - (n_2/F_2) \tan \{(p_2 - 1) \pi/2\} \dots\dots(6.3).$$

For any assigned value of  $p_1$ ,  $p_2$  may thus be calculated; then

$$n = p_1 n_1 + p_2 n_2 \text{ and } l_1/L = p_1 n_1/n$$

as before.

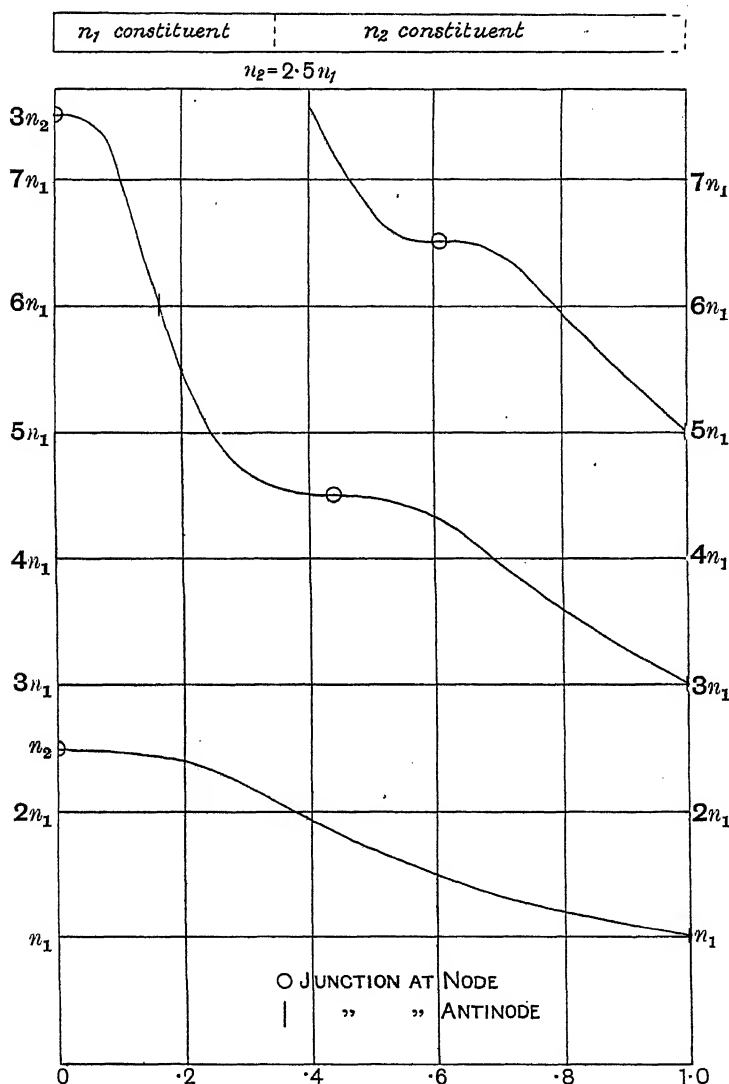


Fig. 3. Frequencies of composite column with a node at one end, an antinode at the other, for various positions of the junction.

For the fundamental,  $p_1$  varies from 0 to 1 while  $p_2 - 1$  varies from 0 to -1 and  $p_2$  from 1 to 0. For the first harmonic  $p_1$  varies from 0 to 1, 2 and 3, while  $p_2 - 1$  varies from 2 to 1, 0 and -1, and  $p_2$  from 3 to 2, 1 and 0.

If  $x$  is at a node in the first constituent, (6.2) shows that  $x/L =$  an even multiple of  $n_1/n$ , and if at an antinode  $x/L =$  an odd multiple of  $n_1/n$ .



If  $x$  is at a node in the second constituent,  $(L - x)/L =$  an odd multiple of  $n_2/n$ , and if at an antinode an even multiple.

The junction between the constituents is therefore a node if  $p_1$  in the equation  $l_1/L = p_1 n_1/n$  is an even integer, and an antinode if it is an odd integer.

Fig. 3 gives the frequencies of the fundamental and harmonics in terms of the position of the junction when  $F_1 = F_2$ ,  $n_1 = 100$ ,  $n_2 = 250$ , and it applies with a suitable change of the frequency scale to any case in which  $n_2/n_1 = 2.5$ .

In the graphical diagram Fig. 1,  $B$  now coincides with  $A$  and the angles  $P_1 C_1 A$ ,  $P_2 C_2 A$  are now  $p_1 (\pi/2)$  and  $(p_2 - 1)\pi/2$ . For the fundamental  $P_1$  moves from  $A$  to  $N_1$ ,  $P_2$  from  $A_2$  to  $N_2$ . For the first harmonic  $P_1$  moves over  $AN_1 A_1 N_1'$ ,  $P_2$  over  $AN_2 A_2 N_2'$ .

### § 7. BOTH ENDS ANTINODES

When both ends of the composite column are antinodes and  $L$  is the length of the column, or in the case of a gas column that length plus the corrections for the two ends, we have

$$\xi_1 = a_1 \cos \{2\pi n x / \sqrt{(F_1/m_1)}\} \cos 2\pi n t$$

$$\text{and} \quad \xi_2 = a_2 \cos [2\pi n (L - x) / \sqrt{(F_2/m_2)}] \cos 2\pi n t \quad \dots\dots(7.1).$$

If  $n_1$  is the fundamental frequency for the column composed entirely of the first constituent and  $n_2$  for the second,

$$2\pi n_1 \{L / \sqrt{(F_1/m_1)}\} = \pi \text{ and } 2\pi n_2 \{L / \sqrt{(F_2/m_2)}\} = \pi.$$

$$\text{Hence} \quad \xi_1 = a_1 \cos (\pi n x / n_1 L) \cos 2\pi n t$$

$$\text{and} \quad \xi_2 = a_2 \cos \{\pi n (L - x) / n_2 L\} \cos 2\pi n t \quad \dots\dots(7.2).$$

The conditions at the junction give

$$a_1 \cos (\pi n l_1 / n_1 L) = a_2 \cos \{\pi n (L - l_1) / n_2 L\}$$

$$\text{and} \quad F_1 (a_1 / n_1) \sin (\pi n l_1 / n_1 L) = - F_2 (a_2 / n_2) \sin \{\pi n (L - l_1) / n_2 L\}.$$

$$\text{Hence} \quad (n_1 / F_1) \cot (\pi n l_1 / n_1 L) = - (n_2 / F_2) \cot \{\pi n (L - l_1) / n_2 L\}.$$

With  $n l_1 = n_1 L p_1$  and  $n (L - l_1) = n_2 L p_2$ , this becomes

$$(n_1 / F_1) \cot p_1 \pi = - (n_2 / F_2) \cot p_2 \pi \text{ or } (F_1 / n_1) \tan p_1 \pi = - (F_2 / n_2) \tan p_2 \pi \dots\dots(7.3),$$

which determines  $p_2$  if  $p_1$  is assigned. Then as before

$$n = p_1 n_1 + p_2 n_2 \text{ and } l_1 / L = p_1 n_1 / n.$$

The method of calculating pairs of values of  $p_1$  and  $p_2$  which satisfy the conditional equation (7.3) is identical with that used in calculating Table 1, p. 210. The condition for maximum and minimum frequencies is that  $n_1/n_2$  must lie

between 1 and  $(F_1 n_2 / F_2 n_1)^2$ . The graphical method of Fig. 1 may again be used to obtain solutions of equation (7.3) and to illustrate the variation of the free periods of the column.

## DISCUSSION

Dr D. OWEN referred to the fact that the work described in the paper had originated from an investigation undertaken on behalf of the Safety in Mines Research Council. He wondered how many of those who benefited by the work of that Council would appreciate the significance of the paper if they were to read it, and how many members of the public were aware of the contributions which pure science was making to an important social service.

# A CAPILLARY TUBE METHOD FOR THE SIMULTANEOUS DETERMINATION OF SURFACE TENSION AND OF DENSITY

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**ABSTRACT.** A capillary tube of radius  $r$  is immersed vertically to a depth  $h_1$  in the liquid of density  $\rho_1$  under test. The pressure  $g\rho h$  required to force the meniscus down to the lower end of the capillary and to hold it there is measured. If  $h_1$ , and consequently  $h$ , be varied, a plot of  $\rho h$  against  $(h_1 - r/3)$  gives a straight line from whose slope and intercept the surface tension and the density of the liquid may be inferred.

## § 1. INTRODUCTION

**D**ESPITE the many difficulties attendant on capillary rise experiments for the measurement of surface tension, the method still continues in wide use and, in some of its different forms, is the most important of the methods which provide the surface tension numbers to be found in the leading tables of constants. Some years ago it was pointed out by one of us<sup>(1)</sup> that a great many of the disadvantages attendant on the practice of the method could be swept away by the simple expedient of *forcing the meniscus down to the lower end of a vertical capillary immersed in the liquid under test and measuring, on a suitable manometer, the pressure required to hold it there.* The trouble of cleaning and calibrating the tube is thus reduced to a minimum, the temperature of the meniscus may be taken by means of a thermocouple whose junction is placed in the immediate neighbourhood of the meniscus, the radius of the tube is easily and accurately measured, and the measurement of the "capillary-rise," transferred as it is to the pressure gauge, may be considerably magnified by the use of a special form of gauge, or of a suitable light liquid in the ordinary U-tube manometer.

Measurements of surface tension by a capillary tube method are primarily concerned with the determination of a pressure and a curvature—the density of the liquid under test appears in the ordinary capillary-rise formula simply because the liquid acts as its own manometer. In the method just described the density of the test-liquid enters but incidentally and is required on account of the back-pressure,  $g\rho_1 h_1$ , due to the fact that the meniscus is at a depth  $h_1$  below the free surface of the liquid. Obviously by varying  $h_1$  it becomes possible to measure both surface tension and density.

## § 2. EXPERIMENTAL

The disposition of the apparatus employed is shown in Fig. 1, which is almost self-explanatory. The pressure is adjusted by means of the bottle shown until the lower end of the meniscus is just flush with the plane end of the tube; this setting may be repeated with very great consistency, observation of the end of the tube being made by means of a low power reading microscope. A needle point is adjusted so as just to touch the *horizontal* surface of the liquid under experiment and  $h_1$  is obtained by measurement of the vertical distance between the needle point and the end of the tube. The pressure required to force down the meniscus is given at once from a knowledge of the difference in level between

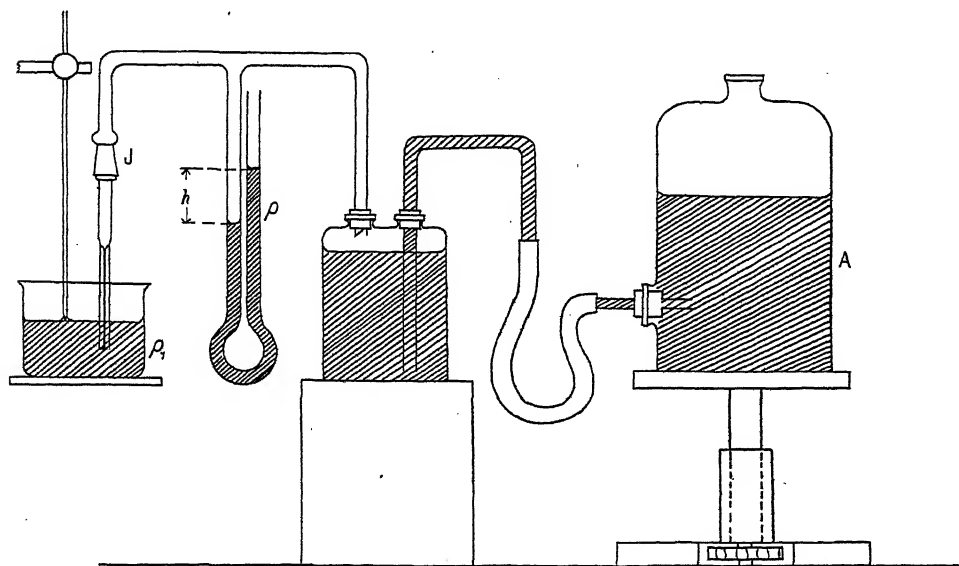


Fig. 1.

the surfaces of the liquid (aniline) in the manometer shown. These last two measurements were made with the help of a vertical-reading microscope carrying a vernier graduated to read 0.01 mm. The radius of the end of the tube was measured by means of a micrometer eyepiece, which eyepiece was standardized by two stage-micrometers, one by Zeiss and one by Baker. These micrometers gave results which were in agreement to 0.003 mm. The density  $\rho$  of the aniline in the manometer was determined in the usual way by the use of a pyknometer.

It is important that the end of the tube shall be plane and that the plane of the end shall be perpendicular to the axis of the tube. This was ensured by placing the tube in a vertical hole, slightly larger than the tube, which was bored in an iron disk shaped as shown in Fig. 2. The tube was fixed in the disk by means of fusible metal, and the central capillary was also filled with fusible metal<sup>(12)</sup>. The tube was then ground down on a glass surface with graded emery and turpentine

until the end was satisfactorily smooth and plane. (The process is considerably assisted by the addition of a little camphor to the turpentine.) It is on occasion found that the fusible metal is strongly adsorbed at the surface of the capillary and an application of hot acid is necessary to clean the latter. The joint shown at *J* in Fig. 1 considerably facilitates the cleaning of the apparatus; it need hardly be said that this joint must be air-tight, and in our own apparatus the fit was so good that the apparatus could be left for half an hour under a pressure of 5 cm. of aniline without showing any appreciable signs of leakage.

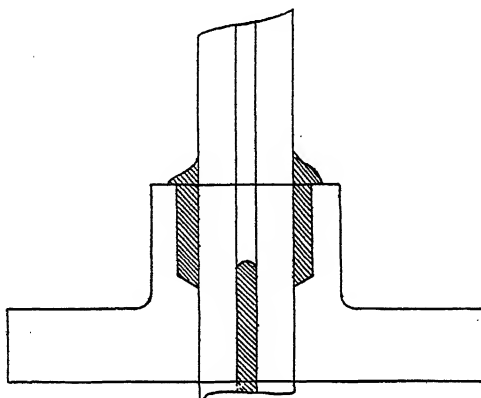


Fig. 2.

The formula for computation is

$$\rho h = \rho_1 (h_1 - r/3) + 2\gamma/gr.$$

It therefore follows that a plot of  $\rho h$  as  $y$  against  $(h_1 - r/3)$  as  $x$  gives a straight line. The slope of this line at once gives  $\rho_1$ , and the intercept gives  $2\gamma/gr$  from which the surface tension  $\gamma$  may be deduced.

### § 3. THEORETICAL

The problem of the determination of the shape of the capillary surface inside a cylindrical tube of small radius has attracted considerable attention. Laplace<sup>(2)</sup>, Poisson<sup>(3)</sup>, Mathieu<sup>(4)</sup> and the late Lord Rayleigh<sup>(5)</sup> are among those who have developed formulae appropriate to this case. At the outset it is necessary to give a clear definition of the term "small," inasmuch as a considerable amount of confusion exists concerning the limits of applicability of such formulae. Thus Richards and Coombs<sup>(6)</sup> have made careful measurements of the surface tension of benzene and other liquids by the capillary rise method and, disturbed by the fact that certain formulae of approximation give impossible results when used outside the limits for which the approximation is valid, have, after indulging in "some mild reflections on the inadequacy of the help afforded by mathematics<sup>(5)</sup>" fallen back on an empirical correction to the simple formula.

If we introduce the convenient notation  $a^2 \equiv \gamma/g\rho$ , so that  $a$  is a quantity having the dimensions of a length, the simple formula

$$\gamma = \frac{1}{2}g\rho rh$$

becomes

$$rh = 2a^2.$$

The criterion of smallness of the radius of the tube is the value of the ratio  $r/h$  or of  $r^2/a^2$ , and the experimental conditions are so chosen that the formulae employed may be developed in ascending powers of  $r/h$ . Paying due regard, then, to the accuracy with which the experimental quantities may be determined, the lowest power of  $r/h$  which may be neglected in comparison with unity is readily observed.

In Fig. 3 below, taking an origin as shown, we have at the point  $P$ , with the notation as in the figure,

$$1/R_1 + 1/R_2 = (y + h)/a^2 \quad \dots\dots(1).$$

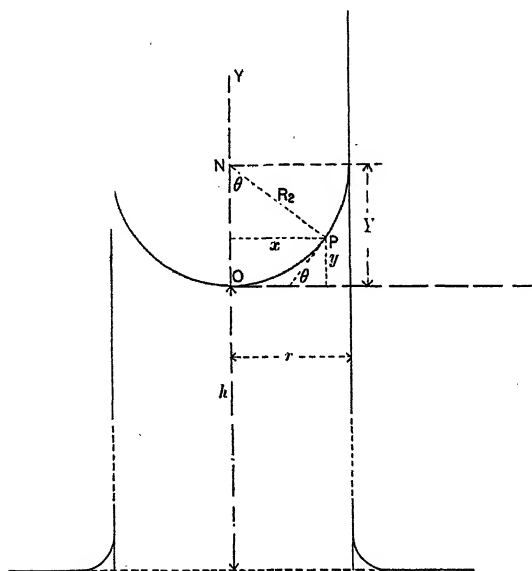


Fig. 3.

Now,  $R_1$  is the radius of curvature of the meridional curve  $OP$  and is equal to  $ds/d\theta$ .  $R_2$  is the second principal radius of curvature and is equal to  $x/\sin \theta$ . Substituting and reducing, we obtain

$$d(x \sin \theta)/dx = x(y + h)/a^2 \quad \dots\dots(2)$$

as the differential equation to the curve. In what follows we shall consider that the contact angle of the liquid with glass is zero.

If we assume that  $y/h$  is always negligible in comparison with unity, two integrations of (2) show that the equation to the meridional curve is a circle. If

we now assume that the meridional curve deviates only slightly from the circular outline so that we may write

$$y = c - \sqrt{c^2 - x^2} + \psi,$$

where  $\psi$  is always small and is a function of  $x$ , Minchin<sup>(7)</sup> shows quite simply, by a modification of Laplace's original method, that

$$y = c - \sqrt{c^2 - x^2} + (c^3/3a^2) \log_e \{(c + \sqrt{c^2 - x^2})/2c\} \quad \dots\dots(3).$$

For a liquid of zero contact angle it is obvious that  $c$  must be identified with  $r$ , the radius of the tube, and (3) becomes

$$y = r - \sqrt{r^2 - x^2} + (r^3/3a^2) \log_e \{(r + \sqrt{r^2 - x^2})/2r\} \quad \dots\dots(4).$$

If we put  $y = 0$  in (1),  $R_1$  and  $R_2$  become equal and the height  $h$  to which the liquid ascends in a tube of radius  $r$  is accurately given by

$$2/R = h/a^2 \quad \dots\dots(5),$$

where  $R$  is the radius of curvature of the meridional curve at its vertex.  $R$  is consequently given by

$$(d^2y/dx^2)_{x=0}^{-1},$$

which value, worked out from (4) and substituted in (5), gives

$$rh = 2a^2 (1 - r^2/6a^2) \quad \dots\dots(6),$$

the corresponding value of  $R$  being given by

$$R = r (1 + r^2/6a^2) \quad \dots\dots(7).$$

If we desire a still closer approximation, it is most readily obtained by equating the weight of liquid raised to  $2\pi r\gamma$ . This gives

$$2\pi r\gamma = \pi r^2 h \rho g + V \rho g \quad \dots\dots(8),$$

where  $V$  is the volume of liquid in the meniscus. But if  $Y$ , Fig. 3, is the ordinate corresponding to  $x = r$ ,

$$\begin{aligned} V &= \pi r^2 Y - \int_0^Y \pi x^2 dy \\ &= \pi r^2 Y - \int_0^r \pi x^2 (dy/dx) dx \quad \dots\dots(9). \end{aligned}$$

Substituting the value of  $dy/dx$  obtained from (4) and remembering that when  $x = r$ , equation (4) gives

$$Y = r - (r^3/3a^2) \log_e 2 \quad \dots\dots(10),$$

we find that  $V = \frac{1}{3}\pi r^3 - (\pi r^5/6a^2) (2 \log_e 2 - 1) \quad \dots\dots(11).$

Substituting in (8) we find that

$$2a^2 = rh + r^2/3 - (r^4/6a^2) (2 \log_e 2 - 1),$$

or  $rh = 2a^2 [1 - r^2/6a^2 + (r^4/12a^4) (2 \log_e 2 - 1)] \quad \dots\dots(12).$

Written in ascending powers of  $r/h$  the equations for  $a^2$ , arranged in an ascending order of closeness of approximation, thus become

$$2a^2 = rh \quad \text{.....(13),}$$

$$2a^2 = rh \left(1 + \frac{1}{3} r/h\right) \quad \text{.....(14),}$$

$$\begin{aligned} 2a^2 &= rh \left[1 + \frac{1}{3} r/h - (r^2/3h^2) (2 \log_e 2 - 1)\right] \\ &= rh \left[1 + \frac{1}{3} r/h - 0.1288 r^2/h^2\right] \quad \text{.....(15).} \end{aligned}$$

This last equation agrees exactly with that arrived at by a considerably longer analysis by Poisson. Rayleigh's result, which is carried far enough to include a term  $r^3/h^3$ , also agrees with equation (15).

To obtain the corresponding approximations for the radius of curvature at the vertex, we note that, *exactly*,

$$2a^2 = Rh.$$

Hence from (12)

$$r = R \left[1 - r^2/6a^2 + (r^4/12a^4) (2 \log_e 2 - 1)\right]$$

and the successive approximations for  $R$  become

$$R = r \quad \text{.....(16),}$$

$$R = r \left(1 + r^2/6a^2\right) \quad \text{.....(17),}$$

$$R = r \left[1 + r^2/6a^2 - (r^4/12a^4) (2 \log_e 2 - \frac{1}{3})\right]. \quad \text{.....(18).}$$

Turning to Fig. 2, we see that if  $R$  be the radius of curvature of the vertex of the meniscus, which is forced down to the lower end of the capillary immersed to a depth  $h_1$  in the liquid of density  $\rho_1$ ,

$$2\gamma/R = g(\rho h - \rho_1 h_1) \quad \text{.....(19).}$$

With the tubes employed it is sufficient for our purpose to assume that  $R$  is given by equation (17). We obtain

$$2\gamma = gr(\rho h - \rho_1 h_1) + g\rho_1 r^2/3 \quad \text{.....(20),}$$

or putting  $b$  for  $2\gamma/gr$ , we have

$$\rho h = \rho_1 (h_1 - r/3) + b \quad \text{.....(21),}$$

and a plot of  $\rho h$  as  $y$  against  $(h_1 - \frac{1}{3}r)$  as  $x$  gives the value of  $\rho_1$  and of  $\gamma$  for the liquid under test.

#### § 4. EXPERIMENTAL RESULTS

Experiments have been carried out on benzene, toluene, acetone, carbon tetrachloride and water. The substances were of first grade research quality and were free from the common impurities. The work was carried out at room temperature, which remained sensibly constant during the half-hour required to take any one set of observations. Tables 1 and 2 below give full details of two typical sets of readings. Three tubes were used during the whole series of experiments having radii of 0.0488 cm., 0.0354 cm. and 0.0237 cm. respectively. From numbers such as those shown in Tables 1 and 2, the graphs of Figs. 4 and 5 were obtained.



Fig. 4 shows, on a large scale, graphs obtained for acetone and for toluene, and Fig. 5 shows the graphs obtained for benzene and for carbon tetrachloride with each of the three tubes. The group of lines for each substance should, of course,

Table 1. Experimental results for benzene

Temperature, 9.95° C. Density of manometer liquid, 1.030 gm./c.c.  
Radius of tube, 0.0354 cm.

Readings for $h_1$			Readings for $h$			$h_1 - r/3$	$\rho h$
Needle point	End of tube	$h_1$	Open end	Closed end	$h$		
9.104	8.696	0.408	6.159	4.240	1.919	0.396	1.976
9.328	8.696	0.632	6.245	4.145	2.100	0.620	2.163
9.585	8.696	0.889	6.345	4.016	2.329	0.877	2.399
10.022	8.696	1.326	6.527	3.848	2.679	1.314	2.759
10.212	8.696	1.516	6.640	3.770	2.870	1.504	2.956
10.428	8.696	1.732	6.717	3.674	3.043	1.720	3.134
10.726	8.696	2.030	6.844	3.526	3.318	2.018	3.417
10.895	8.696	2.199	6.902	3.479	3.423	2.187	3.526

be parallel as the slope is a measure of the density of the liquid concerned. Table 3 gives a conspectus of the results. It must be remembered that the production of authoritative figures is not our primary object, and that the substances used would require purification by redistillation or recrystallisation before any quantitative comparisons of a high degree of accuracy could be drawn.

Table 2. Experimental results for carbon tetrachloride

Temperature, 11.8° C. Density of manometer liquid, 1.029 gm./c.c.  
Radius of tube, 0.0488 cm.

Readings for $h_1$			Readings for $h$			$h_1 - r/3$	$\rho h$
Needle point	End of tube	$h_1$	Open end	Closed end	$h$		
5.811	5.552	0.259	5.911	4.410	1.501	0.243	1.545
6.104	5.552	0.552	6.140	4.180	1.960	0.536	2.017
6.274	5.552	0.722	6.274	4.048	2.226	0.706	2.291
6.453	5.552	0.901	6.422	3.898	2.524	0.885	2.597
6.654	5.552	1.102	6.577	3.742	2.835	1.086	2.917
6.815	5.552	1.263	6.708	3.612	3.096	1.247	3.186
7.140	5.552	1.588	6.957	3.361	3.596	1.572	3.700
7.328	5.552	1.776	7.106	3.216	3.890	1.760	4.002

## § 5. CONCLUSION

To sum up: the method, as the graphs of Figs. 4 and 5 show, is very self-consistent. It is reasonably rapid—about a half-hour suffices to take a set of readings—and while, in common with all capillary rise methods, it takes no account of the possible existence of a contact angle, it overcomes a number of the practical difficulties which are inherent in the ordinary practice of that method.

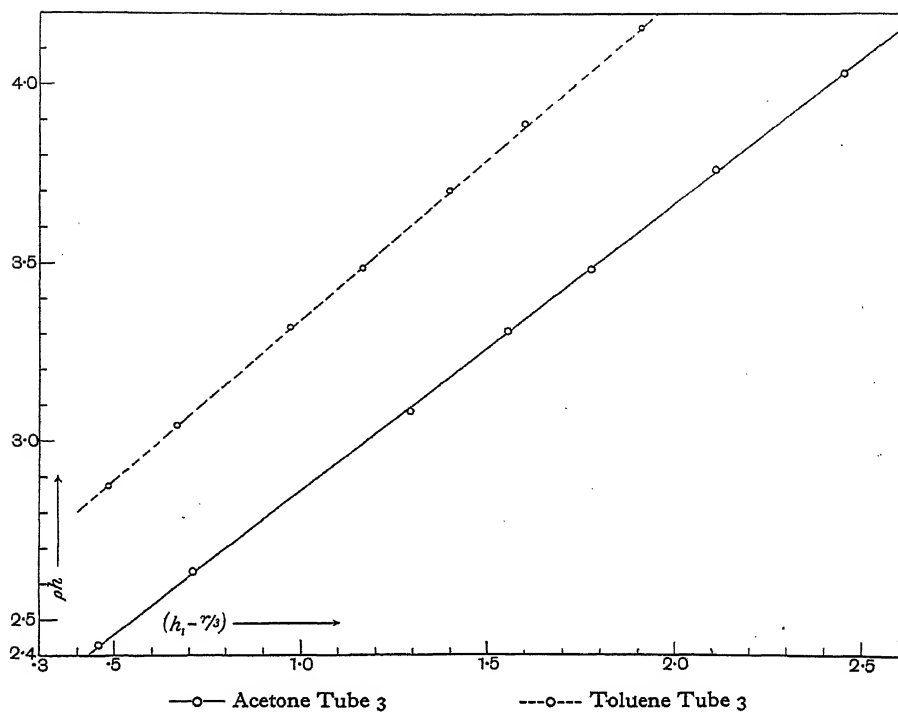


Fig. 4.

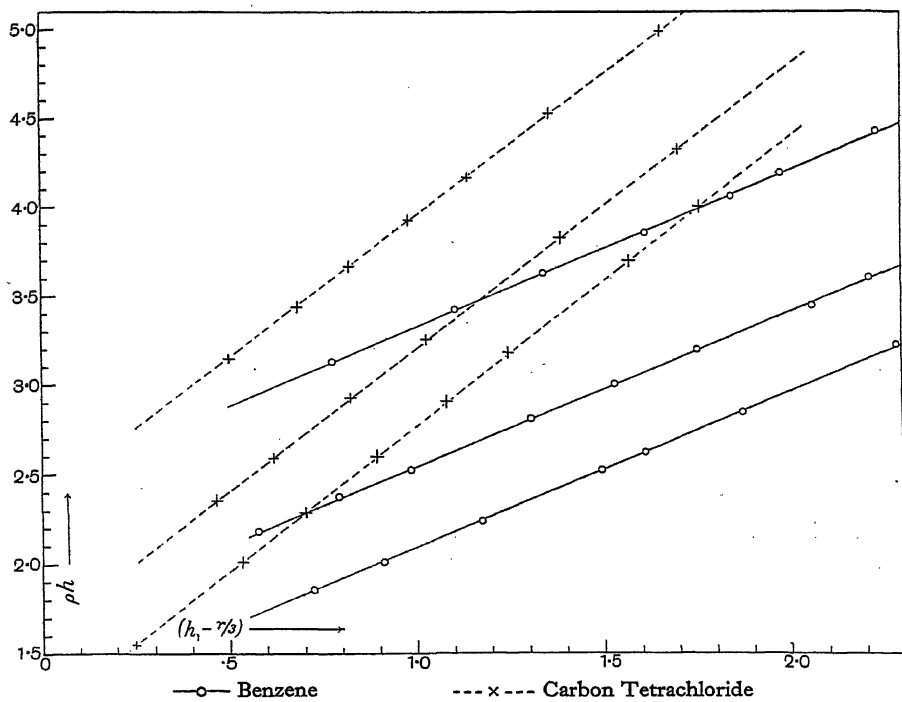


Fig. 5.

With a change of sign of the  $r/3$  term, the method can be applied to the determination of the surface tension of a very small quantity of liquid<sup>(8)</sup>.

Table 3. Conspectus of results

Substance	Radius of tube	$\theta$ (° C.)	$\gamma_\theta$	$\gamma_{15}$	$\rho_1$ from graph	S.G. $\rho_1$ bottle
Benzene	0.0488	16.5	28.94	29.19	0.884	0.8814
	0.0354	16.0	28.97	29.12	0.887	0.8818
	0.0237	16.0	28.47	28.62	0.879	0.8818
Toluene	0.0488	12.1	28.61	28.17	0.870	0.8728
	0.0354	12.0	28.91	28.47	0.867	0.8729
	0.0237	10.3	28.61	28.17	0.866	0.8744
Acetone	0.0488	10.1	24.03	23.43	0.809	0.8034
	0.0354	10.3	24.52	23.92	0.791	0.8032
	0.0237	11.0	23.81	23.33	0.796	0.8026
Carbon tetrachloride	0.0488	11.8	27.36	26.98	1.640	1.603
	0.0354	11.6	27.90	27.45	1.600	1.608
	0.0237	12.8	27.26	27.00	1.600	1.606
Water	0.0488	12	73.98	73.54	1.000	—
	0.0354	19	72.64	73.23	1.006	—
	0.0237	17.7	71.14	71.54	1.006	—

It is our pleasant duty to thank Professor C. H. Lees for the facilities which he has placed at our disposal.

## REFERENCES

- (1) FERGUSON and DAWSON. *Manchester Memoirs*, **65**, no. 5 (1921).
- (1 a) HARKINS and BROWN. *Journ. Am. Chem. Soc.* **40**, 499 (1919).
- (2) *Mécanique Céleste*. Supp. au X<sup>e</sup> Livre (1805).
- (3) *Nouvelle Théorie de L'Action Capillaire*, chap. 4 (1831).
- (4) MATHIEU. *Théorie de la Capillarité*, chap. 2 (1883).
- (5) RAYLEIGH. *Proc. Roy. Soc. (A)*, **92**, 184 (1915).
- (6) RICHARDS and COOMBS. *Journ. Am. Chem. Soc.* **37**, 1656 (1915).
- (7) MINCHIN. *Hydrostatics*, p. 360 (1892).
- (8) FERGUSON. *Proc. Phys. Soc.* **36**, 37 (1923).

## DISCUSSION

Prof. C. H. LEES: We have learned to look to Dr Ferguson for guidance in questions relating to surface tension, and I should like to ask him whether the results for water, which show a decrease of the surface tension as the size of the tube decreases, are sufficiently accurate to be taken as indicating some influence of the walls of the tube on the properties of the surface film.

Mr A. G. TARRANT: I should be glad if Dr Ferguson would tell us whether, in the method under discussion, the position of the meniscus at the lower end of the tube can be located with an accuracy comparable with that obtained in the method, described by him some years ago, in which a small drop of liquid is pressed down in a capillary tube till its lower surface is plane. As I have used this latter

method with excellent results, I should be glad to know whether the present method is capable of equal precision.

Dr D. OWEN pointed out that the title of the paper referred to the determination of density as well as surface tension. Could the method be regarded, however, as giving a measure of density sufficiently accurate for practical purposes?

AUTHOR's reply: I should not like to assume without more extended evidence that the variation mentioned by Prof. Lees was due to adsorption. The question raises an interesting point—that of the determination of the amount of adsorption at a liquid-glass surface by working with a narrow capillary tube in the form of a vertical grid, so that a relatively large surface may be exposed to adsorbent action before the capillary height is finally measured.

The two settings mentioned by Mr Tarrant may be made with about the same order of exactness—both are quite sensitive and satisfactory.

Like the titles of some works of higher art, the titles of scientific papers need not always be taken *au pied de la lettre*. The paper shows, I think, sufficiently well that the surface tension is the important factor, the density determination being of secondary importance—indeed the method may be considered as one which obviates the necessity for a density determination of the liquid under test; this consideration applies with special force to the experiments mentioned by Mr Tarrant, where the direct determination of the density of a cubic millimetre or thereabouts of liquid would not be an easy matter.



scale specially adapted to indicate the specific gravity of light substances such as samples of rubber not exceeding a density of 2.

In order to obtain the required rapidity of operation it appeared necessary firstly to make the weighing in air and water automatic by means of a spring or pendulum resistant, so as to avoid the use of weights, and secondly to dispense with all recording of weights and arithmetical operations, as these greatly increase the risk of error and the expenditure of time required for a determination. A spiral spring resistant has been chosen as being intrinsically much more sensitive than any form of pendulum balance. Owing to the rapidity of the observations, errors due to temperature changes or spring hysteresis do not arise.

The spiral spring used in the instrument has suspended from it a light vertical wire to which is attached a thin circular disc, the sharp edge of which serves as an indicator. The wire terminates in a hook carrying the specimen. The extension of the spring from the zero position of the indicator gives the weight in air, the weight in water, and the difference, namely, the weight of the water displaced. No graduated scale is used in this portion of the instrument.

To perform the operation of dividing the weight in air by the weight of displaced water a special device has been adopted. An inclined bar suitably graduated can be moved vertically so that its zero point can be brought to coincide with the weight-in-air position of the resistant pointer. The fixed unitary length marked off on this inclined bar is always equated to the weight of water displaced by causing the lower member of a parallel rule to pass through the unitary point and through the weight-in-water indication. The upper member of this parallel rule is always slidably located on a knife-edge corresponding in position with the zero of the resistant indicator. This upper member will, therefore, by the principle of similar triangles, cut off from the inclined graduated bar a length proportional to the weight in air, and the number engraved on the graduated bar at the point where the upper member of the parallel rule cuts it will express the relative density of the body under examination. Fig. 1 will make the action of the instrument clear.

To make a determination the zero reading of the instrument must be adjusted by means of the screw at the top of the vertical tube containing the spring resistant. The body to be examined is then hung on the hook attached to the spring. By

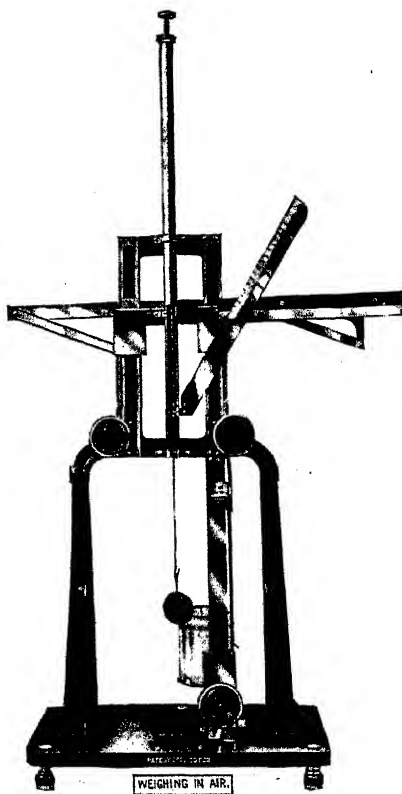


Fig. 2. Instrument for determining the specific gravity of solid bodies.

the turning of the milled knob on the right the pointer attached to the inclined graduated bar is brought into coincidence with the pointer of the spring resistant—now indicating the weight of the body in air. A beaker containing water is raised into position by the turning of another knurled knob at the base of the instrument, thus giving the weight in water. By means of a third knurled knob on the left of the instrument a knife-edge, on which the bottom member of the parallel rule is adapted to slide, is moved to coincide with the weight-in-water indication of the spring resistant. This lower member is pivoted to the inclined graduated bar so that it always passes through the unitary point. The specific gravity can then be read directly on the graduated bar at the point of intersection of the same with the upper member of the parallel rule.

To obtain optimum conditions the graduated scale in the model demonstrated to the Society has a long unitary length, but a scale can readily be fitted to deal with minerals, ores, alloys and other bodies of high specific gravity. Additional springs can be used in dealing with heavy samples. It is easy to obtain determinations accurate to about 0.002, the smallest sub-division being 0.005. A skilled operator can obtain a determination correct to approximately 0.005 in about 30 seconds. In fact, accurate weighing with a first-class balance is necessary to discover any error in the readings of the instrument.

“A Standard Electrostatic Voltmeter and Wattmeter used for Measurements of Alternating Currents at Power Frequencies at the National Physical Laboratory.” Demonstration given by Dr E. H. RAYNER, on February 22, 1929.

The construction of some new apparatus for extending our equipment for alternating current measurements at power frequency provides an opportunity of showing the apparatus before it is installed. The principal instruments are an electrostatic voltmeter indicating up to about 120 volts on a scale about 18 ft. long, and a quadrant electrometer designed for use as a wattmeter and having a similar scale. They are of the type used as the national standards for such work, in which accuracy is of primary importance. As regards sensitivity they must be considerably superior to the commercial apparatus the errors of which it is their purpose to determine. The voltmeter is used commonly at 100 or 110 volts, higher voltages being measured on accurate potential dividing resistances. At 100 volts the scale divisions are about 80 mm. per volt, enabling values to be measured to 0.01 volt over a large part of the range of the instrument. The latter is of the multicellular type, with “needles” specially shaped to open up the bottom and top parts of the scale, which are normally much more contracted than the middle part. The suspension is a bifilar one, fine tungsten wire being used in it. A horizontal aluminium disc in oil provides the damping.

The wattmeter is a more delicate instrument, the torque available being much less than in the case of the voltmeter. Its nominal range is 100 or 110 volts on the “needle” and 2 volts on the quadrants. The needle is of thin aluminium alloy with

stiffening ribs which have been pressed up in it by means of a grooved metal die. Blotting paper is used to press the metal foil into the die under pressures up to 10 tons. No oil damping is permissible. The separation of the quadrants is about 2 mm., and this is sufficiently small to provide, with the grooving of the needle, the necessary amount of air damping. The separation naturally affects the sensitivity, so that the sensitivity, damping and grooving are interdependent. The scale deflection with 100 volts on the needle and 2 volts on the quadrants is about 12 ft. Mechanical adjustments are provided for levelling the quadrants and varying their separation, and for moving them round inside the casing so that they can be oriented in any desired direction as regards the position of the needle. The insulation is made of "amberite." Special calibrating resistance boxes are made for the voltmeter and wattmeter, and selector switches are also required, the one for the wattmeter being of some elaboration, since the needle and quadrants must never be open circuited in passing from one method of connection to another or from one circuit to another.



## REVIEWS

*Physics in Industry.* (1) No. 12, *The Physicist in the Glass Industry*, by Prof. W. E. S. TURNER, O.B.E., D.Sc., F.Inst.P.; (2) No. 13, *Physics in the Food Industry*, by Sir WILLIAM HARDY, M.A., F.R.S.; (3) No. 14, *The Physics of Photography*, by C. E. KENNETH MEES, D.Sc. (Institute of Physics, 1 Lowther Gardens, Exhibition Road, London, S.W. 7.) Paper covers, 1s. net each.

(1) This lecture commences with an historical introduction containing a timely reminder to professional physicists that much valuable work in the glass industry has been done by practical but untrained men. In fact, there was no academic institution for the scientific investigation of glass prior to 1915; since which date, however, much progress has been made in industrial laboratories.

Prof. Turner gives a very informative survey of the physical methods involved, and a few of the topics discussed may be briefly mentioned: (a) viscosity determinations by S. English, of whose apparatus a diagram is given without explanation, although the results are summarized; (b) relation between mobility and temperature, and the importance of annealing processes; (c) optical examination of specimens in polarized light; (d) variation of thermal expansion and electrical conductivity with amount of soda and potash present; and (e) connection between optical properties and composition. Finally an interesting comparison is made of the limits of transmission of vitreous glass and other glasses. Convex glass is said to have a transmission in the ultra-violet as high as that of fused quartz.

(2) The problems of the food industry in which physicists have had some share appear to be those of the control of temperature, humidity and the composition of the air in an attempt to keep the food organisms alive. Uniformity of temperature throughout a space does not seem yet to be attainable.

There is not at present a science of smell, so that a smell cannot be expressed as a number, but Sir William Hardy puts in a strong plea for a method of measuring the concentration of odours. No exact work has been done on the absorption of odours because of the difficulty of measuring concentrations. This subject is of importance in the storage of eggs for example. According to the author much work also remains for the physicist in the problems of conduction in the pipes of cold-storage systems. The remainder of the paper is of a more biological nature, describing the effects of freezing and de-hydration on animal and vegetable tissues.

At the conclusion of a very readable survey reference is made to experiments on cohesive attraction, but the evidently simple diagram mentioned on p. 20 is missing.

(3) This is an important and well-illustrated paper read by the Director of the Kodak Research Laboratory before the Institute of Physics and the International Congress of Photography in July 1928. Some account is given of the progress which has been made in recent years in extending the spectral sensitivity of photographic materials. The methods of studying the relationship between density and exposure both for photographic plates and for printing papers are explained as a preface to a description of the graphic solution of "tone reproduction." There is then a discussion of the "sharpness" of the image, and the common impression that a small grain-size necessarily gives sharpness is corrected.

Other information of great importance to the physicist is contained in an account of the distortion of images of small size. Thus, two neighbouring images become oval in form and appear to attract one another, owing to the spreading of the light in the film. Displacement may also be produced by contraction of the gelatine, and an apparent repulsion between two images appears to be due to local exhaustion of the developer.

It was known, for example, that a weak component between two strong components of a spectral line would not be recorded on a photographic plate, and obviously the similar facts enumerated above are of primary importance to all those who rely on photographic plates for accurate measurements.

These publications may be very strongly recommended to the notice of all scientific workers who desire to know of the methods employed in the varied fields of industrial research and to envisage the problems which still demand investigation with all the help that physical knowledge can give.

J. E. C.

*Physics in Astronomy*, by Sir FRANK DYSON, K.B.E., F.R.S. (Presidential Address to the Institute of Physics, 1 Lowther Gardens, Exhibition Road, London, S.W. 7.) Paper covers, 1s. net.

In this pamphlet, which is largely historical, there is an account of the development of time measurement, with an interesting description of the wireless broadcasting of time signals.

Reference is made to the Shortt clock; which is almost a perfect time keeper except that there is a slight increase in its losing rate. Some new material for the pendulum rod is called for.

Questions perhaps of more interest to the physicist are the development of astrophysics, the Zeeman effect in sun spots, the use of the interferometer for the measurement of giant stars, and the determination of the solar constant. It is very kind of the Astronomer Royal to say that in spectroscopy "an astronomer must be to some extent a physicist if he is to get results of the necessary accuracy."

The whole paper makes delightful reading.

J. E. C.

*Matter, Electricity, Energy (The Principles of Modern Atomistics and Experimental Results of Atomic Investigation)* by WALTER GERLACH. Translated from 2nd German edition by F. J. FUCHS. Pp. xii + 428. (London: Chapman and Hall, Ltd.) 30s. net.

Despite the tragic fate that must inevitably overtake a book on modern physics—for the kaleidoscopic rapidity with which our outlook is changing puts such a work out of date by the time it has appeared on the market—there is no lack of writers who seek to make as plain as may be this fascinating but breathless tale.

Prof. Gerlach's book covers a wide field and is written to make a special appeal, not necessarily to the trained physicist, but to the engineer, the chemist, the naturalist, and to those students of science whose work lies outside the realm of pure physics, and who feel keenly that the changing outlook of the workers in physical science may have important reactions on their own work.

This review would become a catalogue if one were to quote fully the headlines of the thirty more or less independent lectures which make up the book. There is, as one would expect, much stress laid on the experimental side of "atomistics"; and isotopy, atomic rays, disintegration, the electronic charge, the magneton, super-conductivity, various and varied spectrum studies, the photo-electric effect, radiation measurements and, finally, atomism and macrocosm form but a section of the topics treated.

Does the book fulfil its purpose? With a certain amount of qualification, we may say that it does. The experimental side, as one would expect, is well and fully treated, and there is, of set purpose, an almost complete absence of mathematical proofs in the book. This is, we feel, an error of policy, for a simple mathematical exposition saves an immense

mass of verbiage, and nowadays mathematical knowledge forms an essential part of the equipments of the chemist, the engineer and even of the naturalist.

The author has sought a certain measure of stability for his work by concentrating on fundamentals, but changes will happen for all that, and even in the matter of fundamentals there has been a great alteration in outlook since 1926; but, making due allowance for this and for the prolixity involved in the non-mathematical treatment of the topics, we feel justified in saying that each of the lectures forms a very convenient centre from which to proceed to wider discussion and reading.

The translation reads a trifle heavily. Archaic words such as "impartation" (p. 185) give an almost theological flavour to certain parts of the exposition, and (p. 164) "Boltzmann's equation  $P \propto e^{-E/RT}$  enables us to state..." is jargon.

A. F.

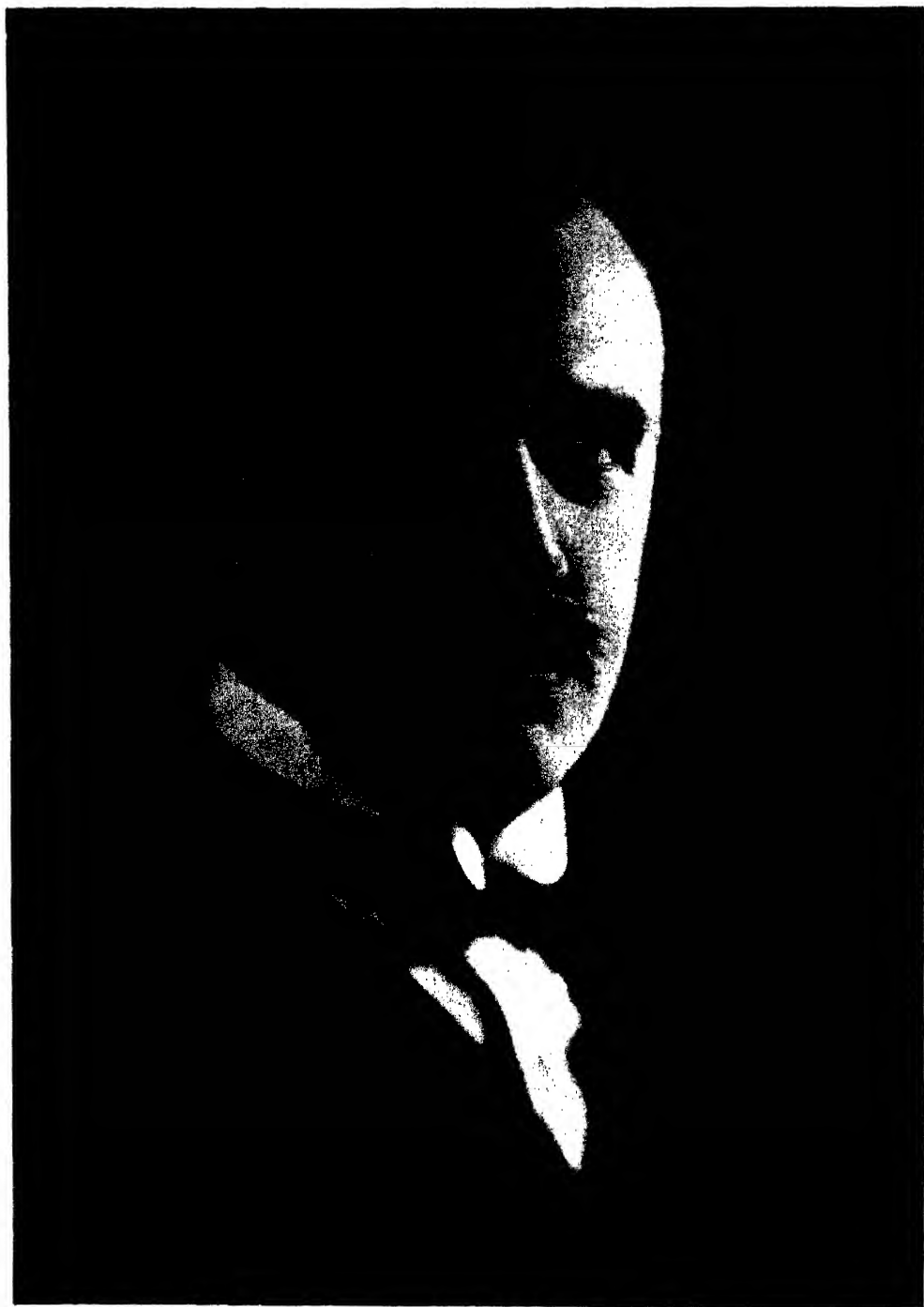
*The Origins and the Growth of Chemical Science* by J. E. MARSH. Pp. x + 162.  
(London: John Murray.) 5s. net.

Mr Marsh is not in the position of the Needy Knife-Grinder—"Story, God bless you, I have none to tell, Sir"—he has an interesting tale to tell, and he tells it in an interesting manner. He does not, save in an incidental way, concern himself with origins, spending much more space on growth, sketching with clearness and philosophic breadth of view the development of chemical science from the far-off days of the four elements and the hypothetical principles, through the theories of phlogiston, salt-formation, radicals and types to these lively present times of co-valencies and contra-valencies, atomic numbers and isotopes.

The book is enlivened—though not overweighted—with touches of interesting biographical detail; and it is with more than academic interest that we look back to those robust days when Liebig, writing of Dumas' analysis of chloroform, could say "Wenn Herr Dumas erklären würde dass er ihn durch die Analyse und zwar mit Genauigkeit bestimmt habe, so halte ich das für Charlatanerie." Other times, other manners!

A. F.





W. H. ECCLES, D.Sc., F.R.S.

*President 1928-1929*

# THE PROCEEDINGS OF THE PHYSICAL SOCIETY

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## THE NEW ACOUSTICS

*Presidential address delivered by*

W. H. ECCLES, D.Sc., F.R.S.

March 22, 1929

IT is just over fifty years since Lord Rayleigh published his *Theory of Sound*. Although it was mainly a mathematical treatment of the subject it comprised much experimental matter and was undoubtedly the most comprehensive work on acoustics that had till then been published. It constituted a treatise of the whole physical theory and in it was arranged in logical order a great mass of material collected from all sources. Many old lacunae in the subject were filled by the author's own original work, experimental and mathematical; and as a consequence we may take it as representing the whole of the physical acoustics of fifty years ago.

The second edition appeared about eighteen years later, and was more than half as large again. Much of the new matter was original, especially that relating to the vibrations of plates and shells, to the influence of viscosity on wave motion, to the phenomena of jets, and to the facts and theories of audition. This edition, taken together with the great treatise of Helmholtz on *The Sensations of Tone*, may be regarded as giving a fairly complete view of the acoustical sciences of a generation ago.

Since the publication of these classical works many briefer theoretical treatises and articles in encyclopaedias, in various languages, have appeared; these have been less condensed or less profound than the classical works, but have for the most part been based upon them. I need refer here to only one of these, the indispensable *Dynamical Theory of Sound* of Prof. H. Lamb, which, like Rayleigh's *Theory*, will endure for years because it rests so firmly on unimpeachable mechanical principles. But all of these books carry the subject along in the traditional manner and show little indication of the change in treatment that has transformed acoustics within the past decade.

During the past ten years acoustics has increased its bulk and scope enormously in consequence of the development of new methods of investigation. On the one hand the range of the frequencies with which the subject was formerly concerned

has extended into regions beyond audition—into the supersonic region and also into that of very low frequency air pulses. On the other hand, acoustics has added to itself a new area, called electro-acoustics, which is based on the telephone and its lineal descendant the loud speaker. The intimate connection with electrical science which has been brought about by the study of the telephone has reacted upon the older and more formal science of acoustics by adding a new technique, new ideas and a new jargon for expressing these new things.

The advent of these novelties has been expedited, perhaps even provoked, by the attention given to acoustics during the war; but perhaps the chief single cause of the practical importance now accorded to acoustics is the rise of broadcasting. This new popular diversion has greatly extended and altered the study of acoustics; it has jerked this study off its accustomed academic paths on to so-called practical lines. That is to say, the study of acoustics is now most keenly pursued, not for its intrinsic scientific interest alone, but also because of its utilisable results. Though this may be regretted by some, it is a fact that ought to be taken note of; and my main purpose in addressing you this evening is to draw your attention to this change of attitude and to suggest that we of the Physical Society ought to give earnest attention to these new tendencies as affecting the future development of this branch of physics.

Looking at the experimental side first, we find that many changes in the subject arise principally from the introduction of new apparatus. Most of this apparatus is electrical; and on account of this fact we have arrived at a state of things in which nearly all quantitative acoustic measurements are made after the sounds dealt with have been converted into electrical currents by means of the instrument named—very badly—a telephone transmitter or microphone. This mode of conversion has been familiar for more than fifty years; but not until recent times have types of microphone been developed which could translate sound into currents without great distortion of some kind or other.

Of these pieces of apparatus the refined condenser microphone, which depends upon the variation of electrical capacity caused by air pressures deflecting one plate of the condenser, is the most noteworthy instrument. But it would have been almost useless without that modern universal instrumentality, the triode amplifier. The modern amplifier is a marvellous tool. It can be constructed so as to magnify electrical currents and voltages conveying powers less than  $10^{-10}$  watt. It can, if desired, amplify these minute fragments of electrical power, say  $10^{11}$  times; and amplifiers can be designed to accomplish such feats at frequencies below the audible range and above the range as well as within it. Evidently, the combination of a sensitive microphone and a high amplifier solves the problem of converting even a feeble pressure variation in air into a measurable electrical current of equal frequency. As a fact it is now possible to detect variations of air pressure of acoustic frequency which are too faint to affect the most sensitive ear.

Not only detection but also production of air waves has been made easy by application of electrical science to experimental acoustics. It has long been possible to convert electrical currents of acoustic frequency into sound waves by aid of a

so-called telephone receiver. Of recent years it has become possible to produce electrical currents of any desired frequency and to vary the frequency easily. By means of electric amplifiers such currents can be magnified before being converted into sound by the telephone receiver. Thus it is possible now to produce sound waves which are smoothly variable in frequency and in intensity through and beyond the range of human audition. In contrast it is possible also to produce, by aid of a tuning fork or quartz crystal maintained in vibration by a triode, sounds of great constancy in frequency and intensity. All these aids to research and practice constitute another triumph of the triode which is too well known to describe here.

In this category of the aids that electrical apparatus have introduced into experimental acoustics we must not forget to include electrical filter circuits. These can be designed to pass currents higher than a given frequency or lower than that frequency, or currents between or outside two frequencies. Once sounds are converted to currents this apparatus can be employed to sift out and purify sounds of various frequencies. The power and scope of this addition to the facilities of the acoustic laboratory have to be experienced to be appreciated fully.

These are the main pieces of apparatus that electrical science has thrust into acoustics. But, in fact, when a sound is converted into electrical current, the whole equipment of the electrical laboratory, from the Wheatstone bridge to the coherer, becomes available for measuring. Nearly all the modern additions to acoustic knowledge are implicitly indebted to this fact.

Besides these tangible adjuncts to the technique of experimental acoustics, electrical science has brought subtle assistance to the more theoretical aspects of the subject. This comes about because vibration phenomena of all kinds approximately satisfy the same linear differential equations. Inasmuch as the study of electrical vibrations in well-defined electrical circuits is easier and has been more cultivated (for practical purposes) than that of air vibrations, acoustic science profits from electrical by a free exchange of ideas about vibrations. Many acoustical problems can be translated into problems concerning electrical networks, and as there exists a great body of knowledge of such networks, the problem is often solved in the act of translation. Further, by adopting the phraseology of the electrician into acoustics, so that translation of the acoustic problem into the electrical problem becomes automatic, a language for thinking and talking becomes available and is found to clear the mind and assist reasoning. Moreover, where some new conception occurs in electrical vibration theory, we can immediately seek the analogy in sound. For instance, Van der Pol's recent discussion of the mode of vibration which he calls a relaxation oscillation and which is exhibited by the flashing neon tube in a resistance-capacity circuit translates into and explains certain features of such acoustic phenomena as the squeak caused by rubbing a slate pencil up a slate (beloved of schoolboys when slates were slates). Some of these advantages are perhaps despised by the acoustic purist, who thinks that the introduction of these electrical analogies into acoustics is merely for the purpose of supporting the electrical expert in an unaccustomed terrain; but as a fact, electrical analogy has been used by the greatest of the pure acousticians, such as Rayleigh and Lamb, and therefore the



gibe need not be feared or regarded. Rayleigh, it was, I believe, who introduced the conception of the acoustical conductivity of an orifice in a rigid barrier.

I propose to summarise rapidly some of the outstanding advances that have accrued in consequence of the new attitude towards acoustics and the new experimental technique. First I will glance at the subject of architectural acoustics—the properties of sound waves in an auditorium. This study has been greatly assisted by the ability to produce pure monotone sounds by passing a filtered alternating current into a loud speaker; and by being able to employ nearly distortionless microphones and amplifiers for picking up sounds of all ordinary intensities and pitches. The fundamental conception, first stated I think by W. C. Sabine, is that a sound created in a closed room is ultimately distributed by repeated irregular reflections so that (leaving foci out of account) each cubic centimetre of air is traversed by waves proceeding in every direction. He clearly stated that sound can only decay by absorption in the walls and furniture and he showed that in general there were several hundred reflections before the echoes die. It has long been known that when the decay is unduly slow the acoustics of a room are defective and the defect is now called reverberation. Sabine introduced the idea of measuring the reverberation time of a room, and defined the duration of reverberation as the time taken for a sound of a million times that of bare audibility to die down to its threshold value. This definition was given, and Sabine made measurements of the reverberation times of rooms, before modern electric methods came to the aid of acoustics—but the subject attracted little attention. Since the arrival of the amplifier, however, the subject has sprung to life in every country. Accuracy has been introduced into our prescriptions of the best reverberation value for speech, for singing, for instrumental music, respectively, and in halls of various sizes. The acoustic data of some of the principal concert halls and debating chambers of the world have been determined and published; empirical laws connecting the optimum reverberation values with the volume of these halls have been established; and the absorption of materials and of objects placed in rooms has been determined by methods based on Sabine's definition of reverberation. As a consequence it is now possible to measure the defects of a given auditorium and to calculate with fair certainty the amount of absorbing material that should be permanently introduced to correct these defects. Better still, it is now easy to plan buildings before their erection to have a desired reverberation time—in fact to be of good acoustic quality; and the design of noise-proof houses and laboratories has progressed very rapidly.

As another example of the range and power of the new methods, take the growth of psychological acoustics. Firstly, we now have firm data of the intensity range of the ear. At a frequency of 2000 cycles the minimum audible sound, according to Fletcher, corresponds with a pressure of  $6 \times 10^{-4}$  dynes per sq. cm. and an amplitude of  $2 \times 10^{-9}$  cm.; while pressures up to 6000 dynes per sq. cm. and amplitudes up to  $1.7 \times 10^{-4}$  cm. are still recognisable as sound. Changes of intensity of a monotone, we now know, cannot be perceived under most favourable conditions unless they exceed 10 per cent. of the original; and thus the total audible range of intensity can be traversed in about 270 barely perceptible steps. Taking comfortably

perceptible differences of intensity, it has been suggested that 120 equal percentage steps may be arbitrarily assumed to cover the range from faintest to loudest sounds. Thus 120 degrees of a sensation scale have been adopted in some quarters as corresponding to the whole range of the ear; and consequently if one sound contains  $x$  times the energy of another, the sensation ratio is  $10 \log_{10} x$  degrees. In Sabine's method of reverberation, if we take threshold audibility as zero his standard initial intensity of the test sound is 60 degrees higher on the sensation scale.

I must refer here to the other method of approach to these new ideas relating to the measurement of the sensation of sound. It has long been obvious that we may measure either the energy flow that causes the sensation, or, alternatively, the strength of the sensation. The measurement of this strength is rightly a psychological problem, and the main suppositions in attempting such measurement are that changes of sensation can be compared with some accuracy and that our perceptions of such changes are related to the energy changes by the rule that equal steps of sensation correspond with equal percentage rises of the power causing the sensation; a geometrical progression in power corresponds to an arithmetical progression in sensation. In other words the logarithms of the steps in power may be used as the measure of steps in the corresponding sensations. This recalls the mode of expressing stellar magnitudes.

Telephone engineers for some years have been using a very convenient standard of change of aural sensation called the 800 cycle standard mile. It is the step in sound sensation which is perceived by an observer when he compares two equal telephones, one at the input end and the other at the output end of a mile of standard cable, the frequency being 800 cycles—the difference of strength of sound being due to electrical dissipation in the (artificial) cable. This step in sensation corresponds approximately to a step of 25 per cent. in power. Hence has arisen a proposal to standardise a power step of ratio  $10^{0.1}$  (which is equal to 1.259) and to generalise it so as to apply it to express the ratio of two powers of any nature and any frequency. The corresponding standard step in sensation is called a "transmission unit," an unfortunate misnomer. It can be calculated from any given set of measurements by taking the logarithm of the power ratio to the base 1.259, or, what is the same thing, taking the logarithm of the power ratio to the base ten and multiplying by ten. We therefore have the following relations between the ratio of the powers causing sound sensations and the number of standard steps of sensation by which the sensations differ.

Power ratio	1.259	2	4	10	100	1000
Steps in sound sensation or "transmission units"	1	3	6	10	20	30

It is interesting to note that that other important subject-matter in psychological acoustics, the sensation of pitch, proceeds by ratios; and, moreover, that the makers of keyboard instruments have adopted, without knowing anything of logarithms, a logarithmic scale for their instruments—equal distances along the keyboard represent equal ratios in pitch. Consequently we conclude that the most human

way of representing acoustical response relations graphically is to use transmission units for intensity as one coordinate and logarithms of frequencies as the other coordinate.

In the acoustics of the ear one of the most remarkable applications of the new technique is that of Wegel and Lane in a research which carries to a well-defined conclusion the observation of A. M. Mayer in 1876 that "no sound, even when very intense, can diminish or obliterate the sensation of a concurrent sound which is lower in pitch." This qualitative observation has now been made quantitative, and though it proves to be a much more complicated matter than Mayer thought, it is broadly confirmed. Low tones are easily masked if not much lower than the masking tone (except in so far as beats may enter) and are not easily masked if much lower than the masking tone; and high tones can be masked by low tones when the ratio of the intensity of the latter to the former reaches a definite value. Wegel and Lane have separated the type of masking which occurs in the ears from that which occurs in the brain. The same investigators have applied their methods to the successful unravelling of old problems concerning combination tones arising from the non-linear response of the ear.

The advances just described in our knowledge of the acoustics of buildings and of the mode of operation of our ears, have led to or aided many noteworthy practical applications. The most important of these is, possibly, that of magnifying the voice of an orator so that it may be made audible to large audiences. The equipment is simple in appearance—a microphone, an amplifier, and a loud speaker—but its development to its present nearly perfect condition has involved much labour. In rooms and halls the problems of echoes and foci, of resonances and reverberation, all tend to be exaggerated by the magnified intensity of the sounds; and electrical vibration of the apparatus caused by waves from the loud speaker reaching the microphone (in addition to the original waves) easily leads either to singing or to distortion. In all cases the demons of distortion obtrude themselves at every stage of the acoustic and electrical processes occurring within the chain of apparatus. The most frequent type of distortion has proved to be that caused by the unequal treatment of sounds of different frequencies, in either the microphone, the amplifier or the loud speaker; but in the study of these public address apparatuses still other types of distortion, originally unsuspected, have appeared. One of these arises from the fact that when a sound is started or stopped a transient vibration of the chain of apparatus, or of the auditorium, may be excited, and this adds itself to the original sound; another trouble may arise from the asymmetric treatment, in any portion of the apparatus but especially in the amplifier, of pure sounds—this introduces sum and difference tones which may cause dissonances in music or unintelligibility in speech. Inasmuch as it is usually found necessary to amplify the wanted sounds until they are ten thousand times as intense as the unwanted disturbing sounds arising from a big audience, the distortions, dissonances and transients just mentioned have placed many difficulties in the path of the development of these appliances for assisting orators. Fortunately the ear is so bad a judge of intensity of sound that exact equality in the magnification of each of the frequen-

cies in a complex sound is not required. In fact certain frequencies of the speech range may be magnified in intensity ten times as much as certain other frequencies in that range, without the ear noticing the inequality of amplification; and certain frequencies may be altogether omitted by the apparatus from the reproduction of a speaker's voice without loss of intelligibility and naturalness. As a consequence of these inherent tolerances in the human ear it is now possible to obtain apparatus capable of helping a public speaker to address great audiences without any suspicion of artificial aid; and apparatus has been developed competent to spread intelligible speech to an audience of a million persons. It has, however, been found better to attempt such feats by dividing the amplified speech currents among a number of well-distributed loud speakers than to deliver it all to one powerful loud speaker; for it is a curious fact that when the intensity of a complicated sound—either speech or orchestral music—is greatly magnified perfectly equally at every frequency—that is to say without any distortion whatever—and delivered to the ear, the listener believes that the sound is badly distorted, partly as a consequence of the non-linearity of the mechanism of the ear.

Just to indicate the closeness of the approach to perfection which these modern applications have reached I might mention that speech sounds ranging from 100 to 6000 in frequency can be magnified fairly equably; and most of the spectrum of the fricative consonants *s*, *f*, *th* between 4000 and 10,000 in frequency can be reproduced. The intensities of the sounds to be dealt with vary in the ratio 1500 to 1 in the case of speech, and in the ratio 100,000 to 1 in the case of music.

And now we must turn to the developments that have taken place in acoustics as a consequence, at least in part, of the introduction of electrical analogy into the theory of sound vibrations. The analogy is possible because the differential equations relating to the transmission of electrical oscillations through electrical networks are linear like those relating to the propagation of sound vibrations. The analogy has long been obvious to the mathematician and may prove of little assistance to him; he may say, justly, that it does nothing other than alter the nomenclature; but even so we may admit that the use of the analogy has helped many recent investigations.

Electrical ideas began to enter acoustics explicitly when the telephone receiver, regarded as an element of an electrical circuit, came to be investigated scientifically. The mathematical aspects of this investigation are very similar to those made familiar to physicists by the study of the vibration galvanometer and various types of electrical machinery such as the synchronous motor. In all cases we have a winding carrying alternating current, a magnetic field acting mechanically on the winding, and relative motion between the two. And when the rotor of a motor or the diaphragm of a telephone is maintained in steady motion by the electro-dynamic forces due to the alternating current, the motion induces an E.M.F. which is proportional to the velocity and may therefore be regarded as due to a special impedance in the windings. That is to say, in the case of the telephone, the inertia, the elastic quality and the energy dissipating property of a diaphragm can, at any given frequency, be represented quantitatively by a hypothetical reactance and

resistance provided the mechanical and electrical units are properly coordinated. This conception is implicit in some of the remarks of Rayleigh and of M. Wien (who, in 1891 equipped a telephone diaphragm with an optical lever and so made the first vibration galvanometer) but it was not until 1912 that it was formulated adequately by Kennelly and Pierce and exhibited in the so-called "vector" diagrams or crank diagrams of the electrician, and given the name of "motional impedance." The motional impedance included, of course, terms or components covering the production by the diaphragm of sound waves or other motions in air. The conception was quickly carried into other branches of acoustics, for instance by Hahnemann and Hecht, and by Webster.

Webster, especially, emphasised in 1914 the use of the conception of acoustic impedance for replacing by a single complex number all the quantities involved in the reaction of an acoustical system. He proceeded to write down formulae for the typical impedances most frequently met with in pure acoustics, namely those due to inertia, elasticity and the production of free waves. He then obtained general expressions for the impedance of the open end of cylindrical and tapering tubes, and incidentally completed, by comparatively easy steps, Rayleigh's early discussion on the properties of horns. His solutions for the conical and the exponential horns are now well known and have been elaborated by a number of followers.

As a consequence mainly of this work of Webster's our knowledge of the operation of horns has been much clarified. At the narrow end of a horn the energy enters in the form of plane waves and so the source works at maximum efficiency; at the open end the reactance due to inertia is minimised and the rate of working on the atmosphere increased by the largeness of the area. Consequently the amount of sound emitted is increased, the waves are little reflected at the open end, especially if their length is small compared with the diameter, and standing waves or resonances are minimised.

What happens to sound waves passing between the narrow end and the open end of a horn depends upon the form of the tubular surface. This has been thoroughly worked out by the methods of Webster and it is well known that the exponential horn, that is, the horn of which the sectional area increases by equal percentages in equal distances, is much better than the conical horn in certain respects. For instance, quoting Flanders, the impedance "looking out" of a hole 0.7 inch diameter in an infinite plane wall, which is variable with frequency, reaches 80 per cent. of its ultimate value at a frequency of 9300 cycles; a certain conical horn applied to the hole brings this 80 per cent. value at 4200 cycles; and a comparable exponential horn brings it at 250 cycles. The horns do not alter the ultimate impedance of the hole in the wall. As a consequence we may treat a horn as having an impedance equal to that of an infinite cylindrical tube of diameter equal to that of the small end of the horn for air vibrations of frequency above a certain lower "cut off" limit which is determined by the geometrical figure and dimensions of the horn. The impedance of an infinite cylindrical tube is, of course, a pure resistance, as energy passes along it from the source undisturbed by reflections from the end.

These new methods of viewing acoustic problems have had many interesting applications. One of these may be briefly described since it has resulted in great improvements in the rendering of music and speech by the gramophone. As is well known the vibrating parts of a gramophone comprise the needle, a lever (called the stylus lever) which rocks on a fulcrum, a diaphragm which forms the back of the sound box, the air chamber of the sound box, the tone arm and the horn. The three first-named items possess inertia and pliancy and therefore contribute to the equations of motion of the system terms analogous to those introduced by inductance and capacitance into electrical equations; the other items contribute only a resistance. To the electrical expert the easiest way of utilising this analogy is to represent the inertia of each part by a suitable inductance coil, its pliancy by a condenser, and its power of consuming energy without phase change by a resistance. The chain of mechanical vibrating elements is thus replaced by a chain of inductances and condensers terminated by a resistance; such an electrical chain constitutes the "artificial line" or the "filter circuit" of the telephone engineer. The properties of these electrical chains have been thoroughly worked out and all the mathematical requirements for ensuring the easy passage of vibrations from element to element without reflection at the junctions are known. Hence can be deduced immediately the appropriate mass and pliancy of the stylus arm, of the diaphragm and of the sound chamber, for the efficient cooperation over a large range of frequencies between these elements and the energy-consuming "load" imposed by the tone arm and horn. The result has been a notable improvement, in both output and quality, of the gramophone, and the instrument is now worthy to deal with the modern electrically-made records.

From this rapid review of the change that has come over the science of sound since the publication of Rayleigh's treatise fifty years ago, it will be seen that the new acoustics is Baconian, that is to say, it is being prosecuted with a view to rendering services to mankind rather than from the motive of scientific curiosity. It is, I think, not being studied so eagerly in this country as in other large countries, notably America and Germany; and I suggest to the Physical Society that this is unfortunate. If this address has the effect of bringing it to the attention of physicists and of prompting those who control college courses and examinations to pay attention to the possibility of encouraging its systematic study, my purpose will have been fulfilled.

# THE DEPENDENCE OF THE MOBILITY OF IONS IN AIR ON THE RELATIVE HUMIDITY

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**ABSTRACT.** The relationship between relative humidity and the mobility of negative ions in air at atmospheric pressure has been examined with a view to possible applications in hygrometric measurements. The method employed was a modification of Zeleny's original method, the end of a wind channel being closed by a disc of gauze fitted with a guard ring through which a steady stream of air of definite humidity was pumped.

The motion of the negative ions due to the action of the air stream was balanced by a counter potential gradient, and the mobility was deduced from the critical potential required to produce a balance. The rate of air flow was measured by means of a Ewing ball and tube flowmeter, a hollow glass sphere being used to make it suitable for low air rates. Efforts were made to construct a direct indicating instrument by amplifying the current sufficiently to obtain deflections on a robust moving-coil indicator, but the variations in the amplification factor were found to be too serious.

## § 1. INTRODUCTION

WHEN time is not an important factor humidity can be measured by the customary methods without the use of elaborate apparatus. It will, however, be recognised that humidity measurements, like most other physical measurements, if rapid observations have to be made, call for apparatus differing radically from that which may be quite suitable if a certain amount of time lag in the instrument is of no consequence. It was desirable, in connection with some special investigations, to have the means of following fairly rapid changes of humidity, and it was suggested that the variation with the humidity of the air of the mobility of the ions produced from some such source as a hot wire might constitute the basis of a method of measuring the humidity. As no information was available at the time as to the relation between mobility and relative humidity, we decided to investigate this effect as a preliminary step in the development of the method.

Zeleny\* had shown that the mobility of the negative ion in dry air was 1.24 times greater than in saturated air, and when the work described in this paper was practically complete Tyndall and Grindley† published their work on the relationship between mobility and the moisture content of the air, using a fundamentally different method.

\* *Proc. Roy. Soc. A*, 46, 238 (1900).

† *Proc. Roy. Soc. A*, 110, 341 (1926).

## § 2. PRELIMINARY EXPERIMENTS

In selecting a method of measurement we had in view the desirability of being able to adapt it later as the basis of the design of an instrument for measuring humidity. The first plan tried was to use a hot wire as the source of ions and observe the variation of the ionisation current between it and a coaxial cylinder when the applied potential was less than that required to produce saturation. The difficulty we encountered with this method was the disturbance due to convection currents from the heated wire. Attempts to use a wire coated with calcium salts so as to obtain an adequate supply of ions at a lower temperature were not successful.

Our attention was then directed to the possibilities of radioactive material. A thin layer of uranium oxide was spread over an aluminium plate and covered with layers of thin aluminium foil, the number of layers being so adjusted that the  $\alpha$ -rays just emerged and produced an ionised layer of gas close to the plate surface. A similar plate was supported parallel to the one covered with uranium oxide, the former being connected to an electrometer. The current passing between the plates for various applied potentials was determined. Owing to the weak ionisation of the uranium salt after filtering through the aluminium foil, saturation currents were obtained with potential differences as low as 10 volts.

While there was no difficulty in measuring the small ionisation currents produced, a very formidable difficulty was encountered in the variable contact-potential effects. With no applied voltage a small ionisation current which varied erratically was obtained. Changes of temperature had a marked influence on the value of the contact-potential, and ultimately this simple method of experiment had to be abandoned in favour of the one described below.

## § 3. WIND CHANNEL METHOD

The principle of the method is to balance the movement of the ions under the electric field by an opposing air blast. In the application of this idea to the design of an apparatus for measuring mobility when moisture is present in the air stream, two sources of error have to be guarded against:

(1) Electrical leakage over the surface of insulators due to a film of absorbed moisture has to be prevented.

(2) Uniformity in velocity distribution across the air stream has to be obtained.

Surface leakage can be reduced to a negligible magnitude if the insulator be kept warm so as to prevent moisture condensation. In these experiments a sleeve was slipped on to the ambroid insulator, and this was heated by a small resistance coil wound round it.

The question of the distribution of the velocity across the air stream was one which received much consideration.

Zeleny in 1898 tried the air stream method. He employed a current of gas flowing through a tube, the end of which was fitted with a disc of gauze which very nearly fitted it. He abandoned the method in favour of one in which the electric field on the ions was perpendicular to the air blast. Now it is a well-known fact



that the velocity of the stream in the vicinity of the walls of a tube falls off to zero at the boundary. Consequently, the air blast method fails if an attempt is made to work with the entire stream which flows through the tube, since there is no opposing blast to balance the electric field in the region of the walls.

By making one modification in Zeleny's original method we were able to adapt it for the determination of the variation in mobility with humidity. Instead of using a single piece of gauze to close the end of the tube, we divided the gauze into a central disc and a guard ring, see Fig. 1. The central disc was made to fit very accurately into the hole in the gauze, but was isolated electrically. (In Fig. 1 the gap between central disc and guard ring has been exaggerated for the sake of clearness.)

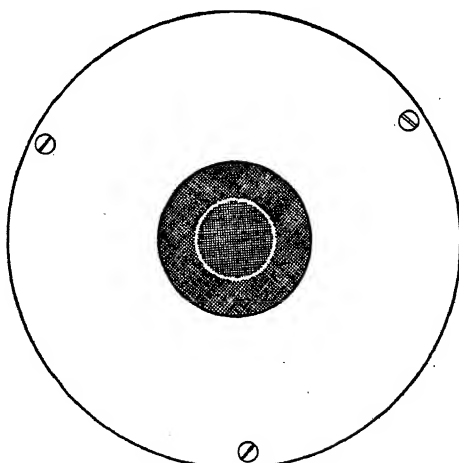


Fig. 1. Gauze electrode and guard ring at end of tube.

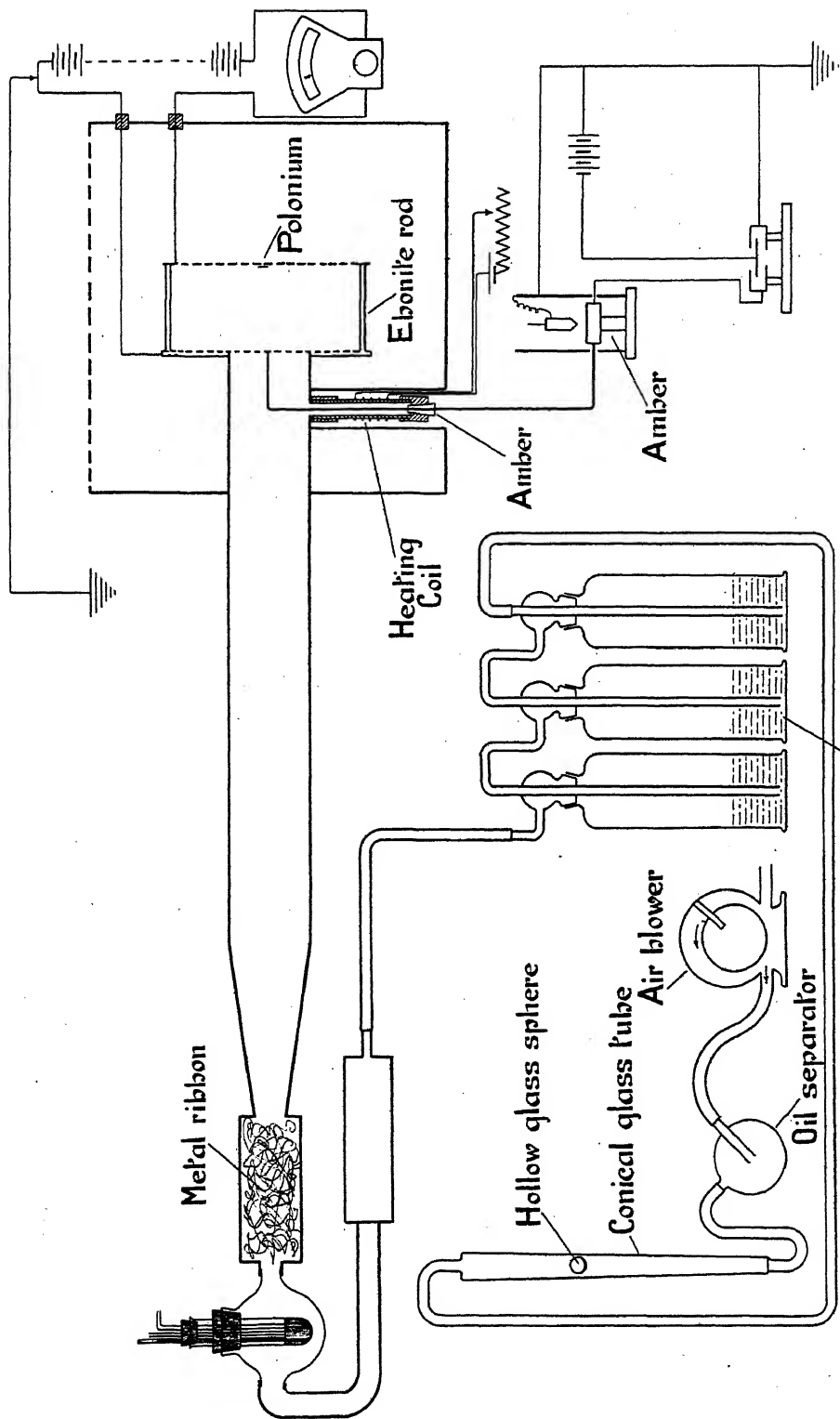
The general arrangement of the apparatus employed in this investigation is shown in Fig. 2. A small air blower delivers a steady stream of gas through three wash bottles in series, containing sulphuric acid solution of definite concentration. The gas then passes through a glass wool filter on to a flowmeter. From the flowmeter the gas passed into a metal tube 2 inches in diameter by 5 feet in length. In one end of this tube a pad made of metal ribbon was inserted and connected to earth. The function of this metal filter was to remove any ions formed by the bubbling of the air through the sulphuric acid solution.

The electrometer and earthing key will be seen in the bottom right hand corner of Fig. 2.

#### § 4. DESCRIPTION OF FLOWMETER

This flowmeter is of the Ewing ball and conical tube\* type, but instead of the usual solid steel ball we employed a hollow glass sphere so as to adapt the instrument to the measurement of low rates of gas flow.

\* Sir J. A. Ewing, "A Ball-and-Tube Flowmeter," *Proc. Roy. Soc. Edin.* 45, 308 (1925); J. H. Awbery and Ezer Griffiths, "Further Experiments with the Ewing Flowmeter," *op. cit.* 47, 1 (1927); *Proc. Phys. Soc.* 39, 296 (1927).



**Sulphuric acid solution of definite concentration**

Fig. 2. General arrangement of the apparatus.

A curious fact came to light in connection with this flowmeter. With the ordinary form of the instrument, when using a solid sphere, it is found that with the tube set vertically the position the ball takes up in the tube for a given rate of flow depends on its mode of vibration transverse to the axis of the tube. When the ball is chattering violently, it is carried to a higher position in the tube than when it is quiescent. This characteristic necessitates using the Ewing ball and tube instrument with the tube inclined to the vertical. The present instrument with the hollow sphere was found, on the other hand, to behave quite satisfactorily with the tube set vertically, and this is to be ascribed to the fact that the sphere is not perfectly symmetrical in form. The walls of the sphere were non-uniform in thickness, and it was observed that when the instrument was functioning the sphere would set itself with the thick lenticular segment lowermost. In this position it rides quite steadily and remains in the axis of the tube with a clear space all around for the air to flow past.

By independent tests it was proved that, to the order of accuracy required, the calibration of the flowmeter did not depend on the relative humidity of the air stream.

#### § 5. METHOD OF OBSERVING

In the experiments the current of gas was maintained constant throughout and the strength of the electric field was varied. Constancy of the gas stream was secured by an observer watching the flowmeter and adjusting the speed of the blower so as to keep the glass sphere floating between narrow limits.

The ionisation was produced by a small quantity of polonium carried on a sheet of gauze, as shown in Fig. 2. Various negative potentials were applied to this gauze and the current flowing across to the disc in the end of the tube was measured by timing the transits of the electrometer spot in the usual manner. The distance between the disc of gauze and the polonium was 10 cm. The disc of gauze was connected to one pair of quadrants of an electrometer through an earthing key of the design shown in Fig. 3. The other pair of quadrants, the guard ring of gauze and the flow tube were all maintained at earth potential. Considerable difficulty was encountered with earthing keys of various types until the form shown in Fig. 3 was evolved, which has proved very satisfactory. This consists of a platinum-faced disc of copper carried on an amber pillar; the disc was connected to one pair of quadrants. A heavy plummet of copper with a solid sphere of platinum set into the end was supported on a thin string above the disc. The plummet was connected to earth. By a lever operated from a distance the plummet could be raised so as to break contact with the face of the disc, thus allowing one pair of quadrants to rise in potential owing to the charge carried by the ions reaching the gauze.

#### § 6. TYPICAL SERIES OF OBSERVATIONS

It is unnecessary to burden the paper with the whole of the experimental data, and the general character of the results will be seen from a study of Fig. 4 which shows a few typical series of observations. The straight lines give the relation between

Applied Potential Gradient

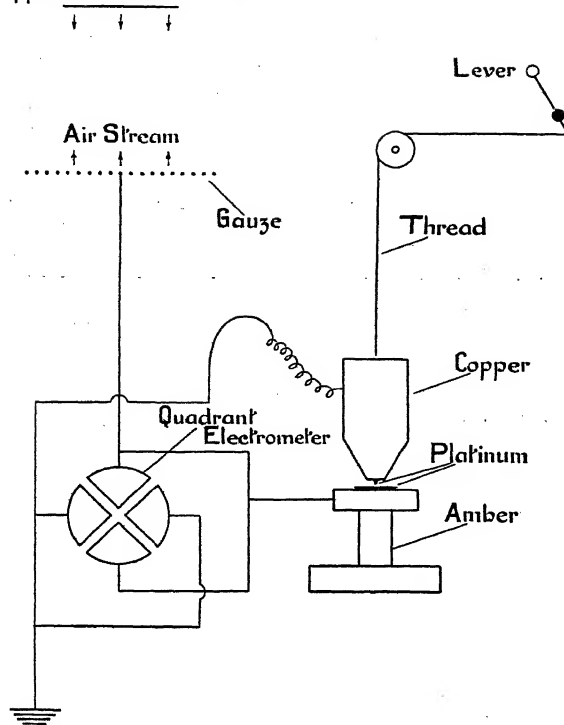


Fig. 3. Connections of electrometer and earthing key.

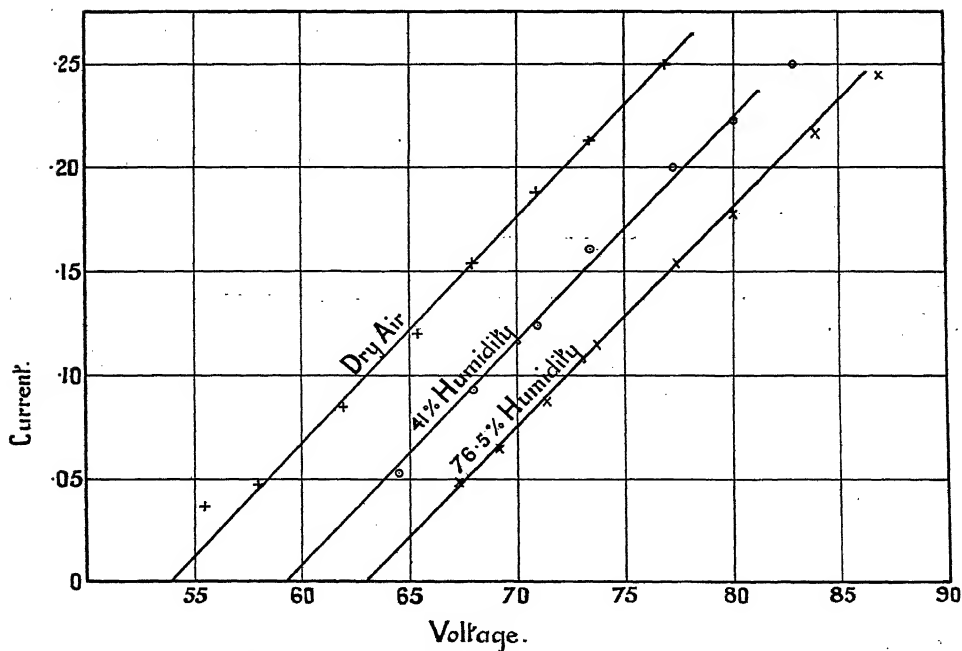


Fig. 4. Three representative sets of observations.

the applied voltage and the current in three separate experiments, using air of different humidities.

The actual balancing electric field was not observed directly, but the intercept on the abscissa was taken as the value of the potential which would set up just sufficient velocity in the ion to balance the velocity due to the air stream.

#### § 7. RELATION BETWEEN MOBILITY AND RELATIVE HUMIDITY

The results obtained in the experiment are summarised in the graph, Fig. 5. The values are expressed in terms of the fractional increment of potential difference required to maintain the same velocity (taking as the initial value the potential required for air which has been thoroughly dried by being passed through sulphuric acid).

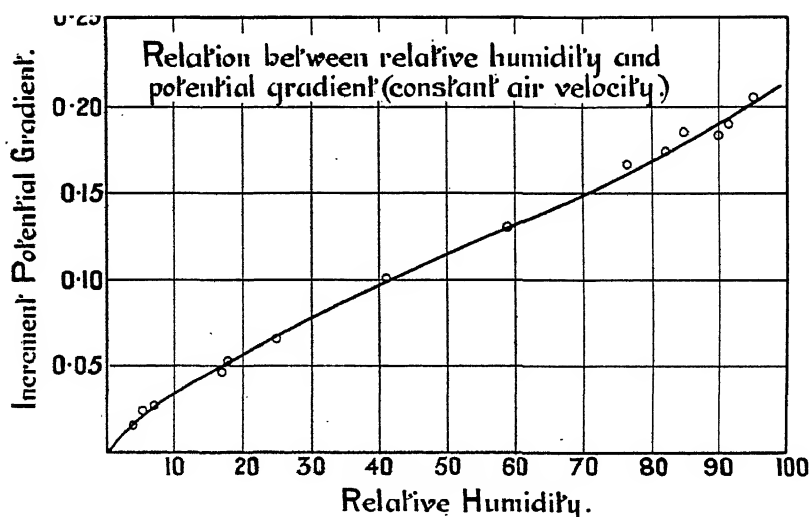


Fig. 5. Variation of the mobility of the negative ion with the relative humidity of the air in which it is moving.

In Table 1 the values taken from Fig. 5 have been converted to relative mobility, taking the value for the ion in dry air as unity.

Table 1

Relative humidity (%)	Mobility relative to mobility in dry air
0	1.00
20	0.95
40	0.91
60	0.88
80	0.86
100	0.82

§ 8. APPLICATION OF THE EFFECT OF HUMIDITY ON MOBILITY  
TO THE DESIGN OF A HYGROMETER

For the purposes of practical hygrometry, the use of a quadrant electrometer as a current-measuring instrument is not feasible. Many attempts have been made to devise amplification devices so as to magnify the minute currents to a sufficient extent to render possible their detection by means of moving coil indicators. A valve amplification system has been tried in this connection, and it was found possible to obtain deflections of the order of 6 cm. on the scale of a microammeter of the pointer type for a change of humidity of 100 per cent. The difficulty encountered with this arrangement was that the amplification factor was not constant and that sufficient magnification could not be obtained to permit of the use of a more robust indicator.

Further developments in this method of hygrometry would be feasible if a more powerful source of ionisation were available, for when the ionisation is feeble surface leakage becomes a limiting factor.

## § 9. ACKNOWLEDGMENTS

The authors desire to express their thanks to Sir Ernest Rutherford, O.M., P.R.S., for the suggestions which led to the investigation: to Dr G. W. C. Kaye for advice on the work: and to Mr A. Snow, Observer in the Physics Department, for his resourcefulness and skilful assistance.

## DISCUSSION

Dr J. H. VINCENT. I should like to suggest the importance of carrying the experiments shown in Fig. 4 to higher values of field. The apparatus seems to be a very convenient tool for investigating many of the still unsolved problems on ions in gases at atmospheric pressures.

Mr K. L. GOODALL (communicated): I should like to ask the authors whether in their search, mentioned in § 8, for an ionisation-current amplification device to replace their quadrant electrometer they have tried the "compensated" valve amplifier bridge developed by Mr C. E. Wynn-Williams?\*. Some experience with this apparatus suggests that it should be suitable for the purpose in view, as it possesses a steady galvanometer zero and a fairly constant amplification factor of about  $10^5$  when power valves are used, permitting the use of a robust low sensitivity galvanometer to measure the amplified ionisation currents.

Reply by Dr EZER GRIFFITHS: In reply to Dr Vincent, I quite agree that it would be of interest to study the form of the curves in Fig. 4 with higher values of the potential gradient. The apparatus described in the paper would probably be quite suitable, but I doubt whether we shall have an opportunity of studying it ourselves. We thank Mr Goodall for his suggestion.

\* *Proc. Camb. Phil. Soc.* 23, 811 (1927).

## SOME PROBLEMS RELATING TO THE MOBILITY OF GASEOUS IONS

BY PROF. A. M. TYNDALL, D.Sc., F.INST.P.

With a note by C. F. POWELL

*Address contributed to the discussion held on March 8, 1929*

**ABSTRACT.** The address deals with the following topics: 1. Established results. 2. The difference between positive and negative mobilities. 3. The effect of vapours. 4. Mobility in pure gases. 5. Positive ions of short age. 6. Suggestions as to future progress. *Note by Mr C. F. Powell:* An apparatus of the "four gauze" type has been designed for experiments with highly purified gases.

### § 1. INTRODUCTION

SOME of the main experimental facts relating to mobility are now from 25 to 30 years old. Yet to-day there is no satisfactory quantitative theory of the motion of an ion through a gaseous medium. Moreover, in recent years some results have been obtained which not only have received no satisfactory explanation, but also, taken at their face value, appear to be mutually inconsistent.

If we omit from consideration for the moment (a) ions in highly purified gases, (b) ions of short age, we may number the following results amongst those which are well established:

(1) The product of mobility and pressure is a constant over a fairly wide range of pressure.

(2) The mobility of a negative ion in most gases as distinct from vapours is greater than that of a positive ion.

(3) The mobility of a heavy ion such as "radioactive recoil atoms" in air is the same as that of ordinary air ions. This is also true for ions formed in hydrogen, carbon dioxide or various vapours, and measured in room air.

(4) The presence in the gas of a vapour with a marked dipole causes a reduction in the mobility of the negative ion and, to a lesser extent, in that of the positive ion.

Under these conditions we may accept the view that the ion is a charged core surrounded by a cluster of neutral molecules. Of the various treatments of the motion of a rigid or "static" cluster which have been given, that of Langevin, while admittedly incomplete, is probably the most satisfactory, since it is not based upon considerations of mean free path. Its consequences have been analysed by Hassé\*.

A truer picture would, however, be given by regarding the cluster as "dynamic,"

\* Hassé, *Phil. Mag.* 1, 139 (1926).

governed by statistical laws and of a virtual size determined by the concentration of neutral molecules in the neighbourhood of the core at any given instant. The expression for its mobility will then include a term which will be a measure of the probability that a given neutral molecule will be found in an element of volume at a distance  $r$  from the charged core. When the drift of the ion due to the applied field is small we are probably justified in applying Boltzmann's theorem by which this probability is proportional to  $e^{W_r/RT}$  where  $W_r$  is the work required to separate to infinity the neutral molecule from the ion.  $W_r$  in turn will depend upon the magnitude of (i) any permanent dipole that the molecule may possess, and (ii) any induced dipole set up in the molecule by the field of the ion. The function  $W_r$  falls off with distance according to the inverse square law owing to (i) and the inverse fourth power law owing to (ii). Whichever view we take of the nature of a cluster, there does not appear to be any strong evidence for supposing that it is equivalent to a layer more than one molecule thick.

For convenience, we may call this term the clustering factor, and its value will depend upon the combined magnitudes of the permanent and induced dipoles in the molecule.

Amongst other factors which we might expect to influence the mobility are:

(a) The mass of the ion ( $M$ ) and the molecule ( $m$ ).

(b) The distance between the centres of a molecule and a cluster at collision ( $\sigma$ ).

For instance, in Langevin's treatment, this enters as a term proportional to  $1/\sigma^2$ .

(c) The density and temperature of the gas.

With a fully formed cluster there is reason for supposing that (a) is of minor importance compared with (b). In Langevin's formula  $M$  and  $m$  enter as a term  $(1 + m/M)^{\frac{1}{2}}$  which tends to unity for large clusters. The experimental evidence suggests that it is sensibly unity. Thus, as stated above, the radioactive recoil ions and air ions have the same mobility in air. The other results under (3) (page 248) suggest that when an ion produced in one gas  $A$  enters another gas  $B$  it sheds the molecules of  $A$  and attaches to itself the molecules of  $B$ . This is to be expected from dynamical considerations. The fact, however, that it makes no difference to the mobility whether the gas  $A$  is hydrogen, a heavy vapour, or the air in which the mobility is finally measured is hardly in accordance with theory. One would expect some difference because the value of  $\sigma$  should vary with the nature of the core. Thus from Langevin's theory Hassé has calculated that the mobility of a hydrogen ion measured in air should be 15 per cent. higher than that of an air ion. This difference is well beyond the experimental error of the experiments. It should, however, be stated that the experiments were carried out in moist gases, i.e. in the presence of foreign polar molecules which tend to increase  $\sigma$ ; they deserve repetition with thoroughly dry gases.

## § 2. DIFFERENCE BETWEEN POSITIVE AND NEGATIVE MOBILITIES

On the static cluster view the difference between the mobility of positive and negative ions is qualitatively explained in terms of the difference in dimensions of the core, in one case a charged molecule, and in the other an electron. With a single



layer of molecules in the cluster both  $M$  and  $\sigma$  are greater for positives than for negatives, and the positive mobility is the smaller of the two. Hassé has shown that in certain gases including air and  $\text{CO}_2$ , Langevin's theory may be applied in this way to give quantitative agreement with experiment, though it is impossible to fit helium and hydrogen into the same scheme.

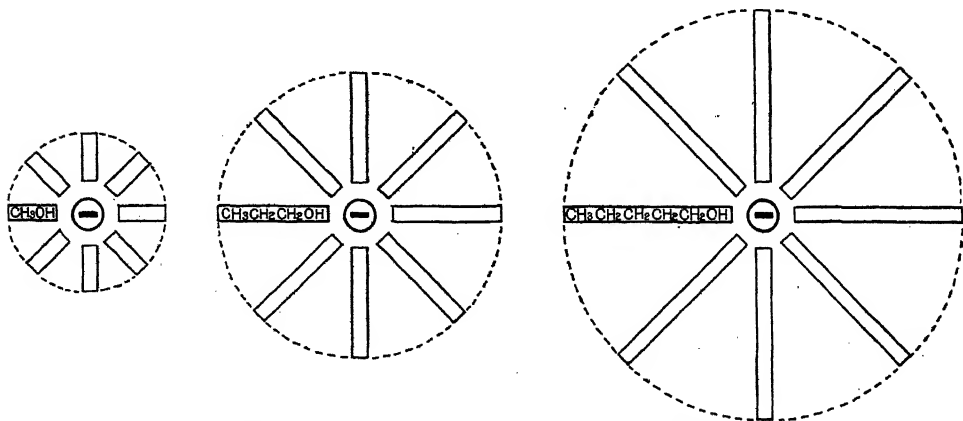
On the dynamical cluster view the lower mobility of the positive ion is not so obvious, because, owing to the fact that the minimum distance of approach to a positive molecule will be greater than that to an electron, the magnitude of the clustering factor will be reduced. Alternative views on this difference have been put forward, namely:

(i) The negative ion may start as an electron and only acquire a cluster after having travelled an appreciable fraction of its path in the measuring apparatus. In this case, its mean mobility would be higher than that for a full life as a cluster. That this is not the explanation is shown by the results obtained by Grindley and the author by a method which was designed, amongst other things, to eliminate any effect of this kind.

(ii) The negative ion is a charged molecule of which the extra electron throughout its path in the measuring apparatus is being transferred from one molecule to another, thus spending a small fraction of its life in the free state. In the author's opinion, this view is scarcely tenable in this form, at any rate for low fields and high pressures. That positive charges are not transferred from molecule to molecule is shown from the experiments with radioactive recoil ions which retain their identity throughout the measurement.

### § 3. EFFECT OF VAPOURS

The effect of vapours with a marked dipole in lowering the mobility of the negative ion is a direct result of the theory. The permanent dipole increases the value of the clustering factor and the polyatomic molecules are of such dimensions as lead to an increase also in  $\sigma$ . This has been shown in some completeness by the



Effective size of ions formed of chain polar molecules.

author and L. R. Phillips\* for the series of aliphatic alcohols which consist of long chain molecules of the form  $\text{CH}_3(\text{CH}_2)_n\text{OH}$ , with a dipole roughly constant for the series and presumably unsymmetrically placed at the OH end. Table 1 illustrates the effect of adding alcohol vapour at 2 mm. pressure to dry air at atmospheric pressure. The table also shows the corresponding values for positive ions. The effect in the case of positive ions is much less and leads to the result that with the higher alcohols (and even for the lower alcohols at greater concentrations) the mobility of the negatives is reduced to a value lower than that of the positives.

Pictorially we might represent the effect for negatives as in the figure, which indicates how the molecules of a long chain polar compound may increase the effective size of the ion. In this case the permanent dipole and the induced dipole are additive. In the case of a positive ion, on the other hand, the sign of the attracting field would tend to reverse the orientation of the molecule, with the result that the binding force would be weaker; fewer alcohol molecules would be found in the layer at any given instant, and the net effect on the mobility would (in agreement with experiment) be considerably less.

Table 1

Added vapour (pressure = 2 mm.)	Mobility	
	Negative	Positive
None ... ..	2.15	1.38
Methyl alcohol ...	1.78	1.28
Ethyl „ ...	1.46	1.26
Propyl „ ...	1.16	1.23
Butyl „ ...	0.88	1.05
Amyl „ ...	0.86	0.96
Decane ... ..	1.98	1.38
Chloroform ...	1.26	1.34
Carbon-tetrachloride	2.0 (2)	1.34

Comparative results which confirm this view were also obtained with chloroform (polar) and carbon-tetrachloride (non-polar), and with amyl alcohol (polar) and the much longer molecular chain decane,  $\text{CH}_3(\text{CH}_2)_9\text{CH}_3$  (non-polar), the non-polar substances having relatively little effect on the mobility of either sign.

#### § 4. PURE GASES

The striking influence of polar impurities cited above is in itself sufficient to emphasise the importance of experiments in highly purified gases. It has been known for some time that, in certain instances where purity obtains, many negative ions do not take on a cluster but remain in the electronic state. This was first found to be the case at atmospheric pressure by Franck† for pure nitrogen, helium and argon, and by Chattock and Tyndall‡ for pure hydrogen. The addition of small traces of oxygen, however, destroyed the electronic character of the ion. Townsend and a number of co-workers have brought forward strong evidence that at lower

\* Tyndall and Phillips, *Proc. R. S. A.*, 111, 577 (1926).

† Franck, *Verh. d. Dtsch. Phys. Ges.* 12, 613 (1910).

‡ *Phil. Mag.* 19, 449 (1910); *Nature*, 84, 531 (1910).

pressures, of the order of several millimetres, the negative ion is always an electron in any non-polar gas, provided that all traces of polar impurity such as water or vapours from ebonite or tap grease be excluded; they regard the loading up of the electron in the experiments at atmospheric pressure as due not to oxygen but to water vapour.

This is a very interesting result, because it suggests that the clustering factor due to the induced dipole is a negligible quantity, and that, therefore, one should expect that vapourless oxygen or air should behave like nitrogen and give electrons even at atmospheric pressure. This has not yet been observed. Starr, Powell and the author\* have looked for electrons in air at atmospheric pressure, taking the same precautions to avoid traces of vapour and with the additional advantage of an apparatus so designed that it was capable of separating the ions, if they were present, into groups of characteristic mobility. While a large number of electrons were found in nitrogen under these conditions, no success was obtained in air.

There is, however, a possible way of explaining the discrepancy, namely, that the air was sealed in a vessel containing polonium. Small traces of ozone and oxides of nitrogen are thereby produced which may act as a polar impurity. The concentration of such impurities will increase with the pressure; at low pressures it may well be negligible even with a continuous source of ionisation.

The results obtained at the Oxford laboratory at low pressure seem to the author to be significant in another respect. If in the absence of polar impurities the clustering factor is negligible because it is only an induced dipole which is operative, then the positive ion should under these conditions be monomolecular. No evidence of this has yet been obtained, but it is conceivable that owing to the longer life of the ion in the medium, even greater precautions to exclude impurity will be necessary before such evidence is forthcoming.

#### § 5. POSITIVE IONS OF SHORT AGE

In the above we have been concerned with ions of relatively long age. There remains the problem of the nature of an ion at short ages. This has arisen from the investigations of Erikson by the method in which the ions are dragged by an electric field across an air blast. He showed that under these conditions there are two types of positive ion—initial and final ions as he termed them—and that the number of final ions grow with age at the expense of the initial ions. The mobility of the initial ion was found to be the same as that of a negative ion which, however, was not subject to the same transformation with age. The author and G. C. Grindley showed that the rate of transformation of initial ions into final ions is retarded by water vapour, the retardation increasing with increase of the pressure of the vapour, and they remarked† that observations in very dry air would be very desirable as the rate of transformation under these conditions might be so great as to be virtually instantaneous.

In order to confirm this view the experiment was repeated by the “four gauze”

\* Tyndall, Starr and Powell, *Proc. R. S. A*, 121, 172 (1928).  
† *Proc. R. S. A*, 110, 364 (1926).

method of Starr, Powell and the author, which as a closed vessel method permits of more thorough drying of the air. No initial ions were then found either in dry air or in pure nitrogen. Further confirmation has recently been obtained by Mahoney who used the air blast method with a closed circuit of dry air; he found no initial ions at an age of 0.0014 sec.\*

This result taken alone would suggest that the initial ion is not a true ion of the gas under investigation, but one which arises from the presence of an impurity. The problem is, however, complicated by the fact that all impurities do not act similarly. Thus the author, Grindley and Sheppard have shown that the rate of transformation is greatly *increased* by ozone. The negative ion is unaffected under the same conditions.

The various possibilities may be put in the schematic form shown in Table 2. In this scheme the ions are called fast and slow instead of initial and final, and it is assumed that in all highly pure gases the negative ion is an electron.

Table 2

	Negative ions	Positive ions			
		Case A	Case B	Case C	Case D
Fast	$\epsilon$	$I_+$	$G_+$	$g_+$	$g_+ + I_1$
Slow	$I_-$	$G_+$	$G_+ + I$	$g_+ + g$	$g_+ + I_1 + I_2$
$\epsilon$ is an electron. $I$ , a cluster of polar impurity.		$G$ , a cluster of molecules. $g$ , a single molecule.			

*Case A.* On this view the transformation would be due to the ion's shedding its impurity members and taking on gas molecules. The arguments against this explanation are:

- (i) In view of the polar properties of the impurity it seems improbable.
- (ii) One would expect that if it were correct the final ion would be the faster of the two; the reverse is the case.
- (iii) All impurities do not act similarly. (See above.)
- (iv) It does not explain the equality of the slow negative and fast positive mobilities, because the two clusters would probably differ in size.

*Case B.* In this case the transformation is due to the collection of impurity by occasional collisions. Indeed, the relatively slow rate of transformation suggests some special type of collision of relatively rare occurrence. In this case the equality of mobilities of slow negative and fast positive ions would be a coincidence. But the action of a polar impurity water vapour in favouring the persistence of fast positive ions does not fit with this view.

*Case C.* This is the suggestion put forward by Erikson himself. It requires, however, the abandonment of our views of a cluster, and at present it has no theoretical support.

\* *Phys. Rev.* 33, 217 (1929). Mahoney remarks in his paper that this result is contrary to the work of the author and Grindley. Reference to the original paper will show that this statement is incorrect.

*Case D.* This alternative is based on the assumption that the true positive ion of the gas at atmospheric pressure is monomolecular and that no samples of gas have yet been experimented upon which are free from some very active impurity  $I_1$ . The transformation would then be due either to the substitution or to the addition of a second impurity  $I_2$ . There is no evidence at present for this view, but it is possible that a still greater degree of purity is essential for the test.

#### § 6. FUTURE PROGRESS

Such difficulties as these convince the writer that the most fruitful line of attack at the present time is so to improve the technique that the nature of the ions, both positive and negative, in pure monatomic and diatomic gases at atmospheric pressure may be investigated under the best conditions of modern vacuum and gas practice. Some surprise may possibly be felt that this has not already been done. But it must be remembered that elimination of small traces of impurities and other experimental precautions become more difficult as the pressure is raised.

With this end in view a new apparatus has been constructed by Mr C. F. Powell in the Wills laboratory at Bristol. Preliminary results of a suggestive character have already been obtained and we are hopeful that they will clear up a number of discrepancies and bring the work into closer harmony with that which has already been carried out in pure gases at low pressures. Not until this is completed can any theoretical examination be conducted upon a secure foundation.

When this information has been obtained, it may still be necessary, in order to discover the real nature of an ion at high pressures, to make experiments by new methods which aim at measuring the mass of an ion and not its mobility.

An attempt in this direction was made in carefully purified hydrogen as far back as 1908 by Chattock and the author\*. The method depended upon the measurement of the minute reduction in pressure set up by the absorption of the ions by a platinum electrode. The results suggested that the positive carrier, which was absorbed, was a singly charged molecule. On the cluster theory this would mean that the remaining neutral molecules were, so to speak, brushed off at the surface and so rendered free to evaporate. The experiment, however, must now be reviewed in the light of our present-day knowledge of surface gaseous films, and the conclusions cannot be regarded as proven.

It is conceivable that the methods applied by Smyth to positive rays at low pressure might be applicable to this problem, but the experimental difficulties would be greatly complicated by the higher pressures required, and the necessity of avoiding such collisions with the molecules of the gas as would lead to the disintegration of a cluster before the ion reached the mass spectrograph.

#### NOTE BY C. F. POWELL

The method employed in the new apparatus, referred to by Prof. Tyndall as having been constructed by me, is the "four gauze" method. This has already been described by Tyndall, Starr and myself†, and was described independently in a

\* *Phil. Mag.* [6], 16, 24 (1908).

† *Loc. cit.*

modified form by Mr van de Graaff\*. It may be regarded in a sense as analogous to Fizeau's method for determining the velocity of light. In the form in which we are using it, it has high resolving power in that, if more than one type of ion is present, each type is represented by a sharp peak in a current-frequency curve, the height of the peak being proportional to the number of ions of that type present in the gas. The age of the ions under investigation is also controllable over a considerable range.

In its earlier form the apparatus was all of metal and was enclosed under a bell jar with external wax seals. In a test with nitrogen it was found that while a large number of the negative ions were electrons, some ions of mobility given by the cluster theory were also present. In its new form the apparatus is free from wax seals and is enclosed in a glass tube. The leads from the various electrodes pass through glass pinches, and the one communicating with the electrometer through a graded pyrex seal. The whole can be placed in an oven and baked out before admission of the pure gas.

Under these conditions of greater purity, we anticipate that we shall obtain nothing but electrons as the negative ions. If this be the case, we are also hopeful that the investigation of the positive ions may be of some interest because, as Prof. Tyndall states, theory suggests that the positive ion may be monomolecular in the absence of all polar impurities. The plant for similar investigations in pure helium is also now available.

## DISCUSSION

Mr J. H. AWBERY. I was most interested in Prof. Tyndall's very clear summary of some of the points which present difficulties in this subject and, like others, I shall look forward with eagerness to the results of the work he is now undertaking on mobilities in very pure gas. There is one objection which has sometimes been urged against any cluster theory of ions, on which some of those present may be able to throw some light. Although there is some disagreement as to the facts, I rather gather from the literature that mobilities do not increase when the electric field is made very high. On a cluster theory, one would expect that sufficiently violent impacts would break up the cluster and lead to a higher mobility.

I would suggest that light might be thrown on some of the problems by further study of the large ions of mobilities about  $1/150$  and  $1/3000$ , which were discovered and studied by Langevin and Pollock, and which seem of late to have received little or no attention.

Mr S. P. MACCALLUM. I should like to congratulate Prof. Tyndall on the great advance in technique he is bringing to the measurement of the mobility of ions at high pressures. His remarks have confirmed the opinion I have had that very few reliable conclusions can be deduced from most of the earlier work. Not much progress can be made until the experiments are made in pure gases and in apparatus in which the gases can be kept reasonably pure. The minutest traces of impurity can in some cases produce a very large effect upon the results.

\* Van de Graaff, *Phil. Mag.* 6, 210 (1928).

We have found at the Electrical Laboratory, Oxford, that a high frequency discharge in monatomic gases is a very effective means of removing impurity when the amount is small. In connection with this method we have also found that amounts of impurity which we were unable to detect with a spectroscope can be detected easily by a measurement of the sparking potential. Circulation over charcoal at liquid air temperature is a lengthy process at high pressures and Prof. Tyndall may find the method suggested very useful.

MR L. G. H. HUXLEY. Mr Awbery has suggested that perhaps under the action of a large electric force the cluster ion would tend to break up, and I believe that some experiments that I have carried out on the corona discharge in helium and neon give some information on this point.

By application of a formula developed some years ago by Townsend it is possible to make an accurate measurement of the mobilities of ions for large values of the ratio of the electric force  $X$  to the pressure  $p$  occurring in the corona discharge. My experiments showed that for values of  $X/p$  of the order of  $\cdot 5$  to  $2$  the mobility of the positive helium ion, when reduced to atmospheric pressure, was about 30 cm. per sec. This is the order of magnitude given by Langevin's formula for a monomolecular ion and is much greater than the number 5 given by Franck and Pohl for small values of  $X/p$ . Similar results were obtained in neon and nitrogen. The positive ions in neon and helium also exhibited an increase in mean free path with increasing energy.

DR D. OWEN. It is a pleasure to hear further of the interesting work on ionisation that is being carried out by Prof. Tyndall and his pupils at Bristol. It is interesting to note that the work on mobilities at normal pressures leads to the definite conclusion that the ions in gases are not single molecules but aggregates. It would be of interest to know whether in the case of positive ions a transition occurs at some stage in reduction of pressure, of the kind which is known to occur in the case of negative ions, being here interpreted as indicating that the ions are electrons which maintain their existence in the free state. Again, from the structure of the polar molecules of the alcohol series  $\text{CH}_3\text{OH}$ , etc., with their exterior positively charged atoms, it might be inferred that the negative ions in a gas containing vapours of these alcohols should be larger and hence of lower mobility than the positive ions, which is contrary to the usual order. Is this actually the case? The increasing importance at the present time of power transmission at very high voltages prompts another question: whether Prof. Tyndall can give any data as to the character of the ions which occur in high-tension discharges?

DR F. J. W. WHIPPLE. A remark made by Mr Awbery seemed to imply that no work had been done in recent years on the large ions discovered by Langevin. That is far from being the case. Prof. Nolan and his school in Dublin have devoted much time to the investigation of the ions of different kinds in the atmosphere. They have demonstrated that the Langevin ions are Aitken nuclei. Roughly speaking, one-third of the nuclei present at any time are neutral; the other two-thirds carry charges positive or negative. These charges are acquired from the

small ions. When the atmosphere is polluted, nuclei are numerous and the small ions are short-lived; conductivity is therefore low and potential gradient assumes high values. The interplay between large and small ions is one of the most important phenomena in atmospheric electricity.

Reply by Professor TYNDALL: In reply to Mr Awbery, I think that the effect of polar impurities may be important at high field strengths, because, owing to the strong attraction, their molecules would be less readily removed from the cluster. The experiments in pure gases cited by Mr Huxley are very significant in this respect. Loeb's deductions from the early form of Langevin's formula and an expression due to J. J. Thomson are based upon a misinterpretation of Thomson's paper. Thomson's paper is an attempt at a statistical treatment of the subject based upon mean free paths; it has not yet, however, been developed to a numerical stage. In the course of the paper he deduces two expressions for the reciprocal of the energy free path, one assuming only elastic collisions, and the other assuming only attractive forces between ions and neutral molecules. These terms must, of course, be added, but Loeb omits the former from his calculation and thereby obtains an expression independent of  $\sigma$ .

There is a corresponding special case of Langevin's 1905 formula which is derived from a treatment of elastic collisions coupled with attractive forces but without involving mean path considerations. Langevin's expression may be written

$$\text{Mobility } (k) = (1 + m/M)^{\frac{1}{2}} \cdot A/\sqrt{\rho(K-1)},$$

where  $A$  is a function of a parameter, the value of which depends upon the relative importance of elastic collisions and attractive forces. When the latter are of much greater importance than the former,  $A$  tends to a limiting value 0.505.

With reference to Mr MacCallum's suggestion of the use of high frequency discharge for cleaning up impurities, I might say that we had considered this possibility, but doubted whether it could be applied to gases at the high pressures we are using. His opinion, however, that it may be practicable even at 100 mm. is very welcome, and brings the method within the range of practicability.

In the case of high tension discharges from transmission cable raised by Dr Owen, we have, presumably, in the glow itself, ions of very short age travelling in strong fields, with, however, complications due to the presence of a high concentration of polar impurities formed by the chemical action of corona discharges. Dr Owen is correct in his surmise that, in the presence of organic vapours, the positive ion may move faster than the negative. I did not state this at the meeting, but reference is made to it in the printed text of the address.

The matter of large ions to which Mr Whipple referred was one of the various subjects omitted for the sake of brevity from the paper. It is an interesting subject of meteorological importance, and bound up with the question of condensation nuclei in the atmosphere. It is full of experimental difficulties, the chief of which is that of obtaining a controllable supply of ions of the same kind which can be repeated indefinitely in a series of experiments.



# THE TEACHING OF GEOMETRICAL OPTICS

*Discussion held on April 26, 1929*

## I. THE NEED FOR REFORM IN THE TEACHING OF OPTICS

BY T. SMITH, M.A.

**ABSTRACT.** The student should not be taught any theory until he has learnt to distinguish between light and sight, and acquired a knowledge of the properties of light, and of the effects observable with optical instruments. In his practical work he should realise the limited powers of unaided and of aided vision, understand why there is always a limit to resolving power, and why numerical aperture is important. He will then realise that the geometrical theory cannot do more than locate "perfect" images. Examples of the failure of this theory outside these limits are given. The wave treatment should be taught as a reliable way of dealing with optical problems generally. The use of simple matrices is advised. In advanced work Hamilton's method is preferred. The sign conventions are as in ophthalmic practice and in analytical geometry.

THERE should be no need to-day to urge the view that no scheme of education which ignores optics can be deemed satisfactory. If reasons for this belief are demanded we have only to mention the importance to each of us in our daily lives of making a right use of the basic facts of vision and of the elementary properties of light; our dependence for many purposes on optical instruments, such as spectacles, cinematograph projectors, field glasses, microscopes; and not least, for those who desire to understand the world around them, the fact that in optics are found some of the more intelligible applications of those ideas, still somewhat strange to those who were learning physics in the 19th century, which seem destined to affect so profoundly the views of that world revealed in the pictures now beginning to be unfolded before us, to make the justice of our claim apparent. The list need hardly be extended. We ought however to observe that the chances of anyone reaching, without instruction, correct views on any one of these items are negligibly small. The need for instruction exists, and since it is not merely to a few specialists that the matter is of interest, much of this instruction should be given in the schools. The first question then to be discussed is the form this elementary instruction should take.

When our Hon. Secretary first mentioned the need for a change in existing teaching, and invited me to give the opening address at this discussion, I naturally asked what optics was taught in schools to-day. His reply was brief but illuminating:

" $\frac{1}{u} + \frac{1}{v} = \frac{1}{f}$ ." I shall have something to say on this equation when I come to deal with lenses. At the moment I only wish to point out that it represents that aspect of lens theory which is least interesting and least instructive. In this discussion we are dealing with the wider subject of optics, and it is not unimportant to observe that optics does not lie entirely within the domain of physics. Physiological optics and the psychology of vision are more interesting and more important

to most people than laws about optical images, and, at all events in the initial stages, these, together with the outstanding physical properties of light, should form the foundation of the course, which ought to be experimental. Perhaps the most important aim at this stage should be to teach the pupil to think correctly about light and sight; the experiments involve both physical stimulus and mental sensation. Our aim is to learn to reason accurately about the former through our experience of the latter. The laws of these two realms differ, and the task is not as simple as the student may at first be disposed to think. The experiments will generally be qualitative rather than quantitative. Experiments on brightness and colour, persistence of vision, fatigue, glare, and the power and limitations of adaptation to changes in external conditions, with their relation to the exciting light, are typical of the work that might be done early in the course.

In this preliminary stage the student should have realised that the eye is very fallible as a measuring instrument. When it must be employed in this capacity care is taken to use it under the conditions which have been found to suit it best, and ingenious instrumental aids are nearly always employed. The evolution of photometers, to take only a single example, affords a good example of the way in which we have learnt to make effective use of a somewhat indifferent instrument. We have here reached the stage when light has to be considered as a form of energy. The discussion of the two forms in which energy can be radiated, corpuscles and waves, introduces a part of the course which can be well illustrated by experiment. The apparatus used is perhaps not often found in schools, but it need not be expensive. For example replicas of diffraction gratings, suitable for illustrating the periodic character of light and the relation between colour and wave length, can be obtained for a shilling or two.

The student will usually have sufficient qualitative knowledge of the properties of optical instruments like the telescope, microscope, and photographic lens for these to be employed in experiments set up by the master. The aim in the next stage, and the one to which I attach as much importance as any, is to teach the student how to use these instruments correctly. There is here a difficulty which can only be met in the course of time. The proper use of the microscope, particularly with objectives of high power, is of the utmost importance for the advancement of knowledge in several directions, and ought to be taught in school; but there are no teachers. The trouble is that most microscope users are not aware that they do not use their instruments properly—i.e. so as to see everything that the system is capable of showing and avoid false effects (the interpretation of what is seen need not detain us here). Indeed it has been said that all the expert microscopists in the country can be counted on one's fingers. It is chiefly a matter of using the instrument intelligently, taking trouble, exercising patience, and gaining experience. The teacher should have a good practical knowledge of the wave theory of light, and this points to the physics master as the best instructor. A holiday course for science teachers on the use of the microscope, by one of the great masters of the art, would probably be the simplest means of bringing about an improvement. However, we are counting our chickens before the eggs are laid. The microscope and telescope

are used to enable us to see what is beyond the power of our unaided eyes. The first step in a course on the use of instruments therefore consists in experiments on the power of the eye in direct unaided vision. The most important facts to be brought out concern the capacity of the eye to distinguish detail under different conditions. The need for sufficient illumination may be exhibited in many ways. Next the importance of the size of the aperture admitting light to the eye should be considered. If this is reduced much below the natural size of the iris, detail disappears even though the illumination is ample. Quite striking observations may be made with the simplest apparatus. For instance objects containing prominent straight lines lying in various directions may be viewed through a straight cut made in the film of a blackened dry plate. Lines parallel to the cut will appear blurred or even disappear entirely, while those approximately perpendicular to the cut can be seen distinctly. This experiment, with suitable variations, should be used to show that the discernment of detail is dependent upon the use of a light-restricting aperture of considerable size, and that as the aperture is reduced in any given direction the size of the smallest detail we can distinguish in that direction changes in the inverse ratio. A familiar example is afforded by the ability of a photographic lens, which has an aperture much larger than that of the iris of the eye, to record on a photographic plate detail which is invisible to an eye placed in the same position. We also infer, contrary to the generally received opinion, that when a photographic lens is stopped down, the images of objects in sharp focus lose, instead of gaining, in detail. These conclusions will prepare the student to understand the importance of numerical aperture in deciding the smallest detail that can be correctly rendered in an image. The ability of the eye to detect departures from exact alignment of two parallel straight lines, where they cross a third line, should also form the subject of experiment, as the difference between this magnitude and the separation of two points discernibly distinct is of considerable significance.

When instruments are introduced to extend the powers of observation of the naked eye, the experiments on the effect of reducing the size of the aperture should be repeated to demonstrate that the same laws hold. It is particularly important for the student to realise the uselessness of increasing the magnification beyond the value suitable for the aperture actually effective in the experiment. In all these experiments the size of the exit pupil should be measured. The character of the images of simple objects may next be investigated by examination under a low-power microscope. The series should include the image of a star seen in a good telescope, with the objective used both at full aperture and stopped down; and the appearance of double stars on both sides of the resolution limit: in the microscope parallel rulings of various spacings should be examined, and the student should be led on to appreciate the importance of correct illumination. Incidentally the microscope, or rather the microscopes, for there should be several, may be used to exhibit natural history or mineral specimens of optical interest, illustrating for example brilliant coloration due to the optical effects of particular kinds of structure.

I have suggested that the student should gain, in some such way as that just

sketched, a knowledge of the principles involved in the use of optical instruments as well as practice in the art itself, before he is confronted with the special theory of optical instruments. If we have to choose between teaching the use of an instrument and teaching a theory which rarely calls for application, by all means let us select the former. Far more of our students will have occasion to use the microscope as a tool than will ever need to calculate conjugate distances for a thin lens. Knowledge of the kind that has been mentioned is essential for the proper handling of an instrument, but no one would be any the poorer if the equation said to represent present teaching were entirely forgotten and lost. It should be unnecessary to add that the lenses of the telescope and microscopes used in the experiments should be of really good quality. With the microscope particularly it is possible for poor equipment to be worse than none.

Some of the most important properties of light considered as a wave motion have yet to be introduced before we can consider the theory of lenses. They include the constancy of the speed with which light travels, the principle of interference, the qualitative explanation of rectilinear propagation based upon interference, and the dependence of the speed upon the medium and the frequency (which is invariable). From these we can construct a complete explanation of reflection and refraction. The very great value of the speed should be pointed out on account of its importance in leading us to regard our sensations as a function of the stimuli in a statistical sense only. I assume that the instruction now given on all these points is satisfactory.

It may be thought that with the deduction of the rectilinear propagation of light from wave concepts, and the derivation of the laws of reflection and refraction in their geometrical form, the way becomes clear for the discussion of the properties of lenses from the geometry of rays, in the manner with which we are all familiar. I wish to urge the contrary view. I am not aware that anything of physical importance is gained, though I am conscious that much is lost, by introducing the ray idea into the subject. We are in effect adopting, for use in two ill-defined and overlapping sections of optics, two mutually inconsistent theories of light. There might be something to be said for the retention of the geometrical theory in elementary teaching if it possessed greater simplicity, or if it presented a picture more readily grasped by the student's mind: in fact the advantage lies on the other side. In technical optics ray-tracing is an important process, but this does not justify the use still made of rays in teaching the principles of image formation. The ray theory leads to a number of conclusions which are contradicted by experiment. On the other hand observation confirms the predictions derived from the wave theory. If, notwithstanding these facts, we continue to accept the geometrical doctrine, we are false to the professed principles of experimental science. As an exercise in geometry the ray theory is not out of place: as a branch of physics, or in association with "optical," we are bound to object to its use.

The errors which inevitably accompany the geometrical theory are due to the assumption that the direction in which the radiant energy falling on a vanishingly small area of an arbitrary surface is propagated, depends only on the direction of

the normal to the wave surface where it meets this area. The explanation of rectilinear propagation according to the wave theory requires comparatively remote parts of the wave front to exercise some influence, and in fact the explanation breaks down near the edge of a wave or when the wave front is not extensive. This agrees with the observation that detail is lost when the aperture limiting the light traversing the instrument is reduced in size. The geometrical laws of refraction and rectilinear propagation may therefore mislead us through confining our attention to too restricted a part of the wave front. We can readily illustrate the kind of error that a student would be apt to make. Suppose we have a solid circular cylinder, with flat ends normal to the cylinder axis, of a transparent material in which the refractive index is a regular function of the distance from the axis. Consider a ray which enters the cylinder in a direction parallel to the axis. It is undeviated on entering the cylinder because the incidence is normal. The refractive index in the direction in which it is travelling is constant, and the geometrical theory would lead to the conclusion that it would continue to travel through the cylinder in its original direction. The wave theory leads to a very different conclusion. As the refractive index differs at different distances from the axis, the speed of the wave front depends on this distance, that is to say the wave front becomes progressively more and more inclined to its original direction, or the energy is propagated in a curved path. If the refractive index is a maximum along the axis and falls continuously as the radius increases, the path will oscillate from one side of the axis to the other. This example incidentally illustrates the ease with which, on the wave theory, we can discuss the effects of non-homogeneity in our materials—a problem which arises frequently in practical work. As a second illustration consider a wave front after refraction by a lens in the form of a portion of a perfect sphere contracting as it advances towards its centre. In general the area of the wave front when refraction occurs will be sufficiently large to ensure effective obedience to the laws of refraction and rectilinear propagation. As the wave advances the dimensions of the front decrease, and before the focus is reached it has shrunk so much that the conditions necessary for rectilinear propagation are no longer satisfied. We see therefore that the very fact that the light is converging towards a focus implies the failure of those conditions upon which the ray theory relies for its validity. In other words geometrical optics is incompetent to deal with the very phenomena for which alone it exists. It misleads us if we consider by its aid the nature of an image; it indicates the converse of the true effect when the size of the aperture is varied; it gives incorrect laws for the depth of field and the depth of focus; it assigns the wrong position for the best image in the presence of slight aberration; in short it is much more difficult to find a problem to which it yields the correct answer than to extend the list of those in which it contradicts the wave theory. I suggest, in view of these notable failures, that it is essential for us to abandon the geometrical theory of image formation.

There is one method of treating the lens problem, without utilising any theory of light, on which a word of criticism may be made here. The argument used is that every point (let us say on the axis) of the object space has a unique image in the

image space, and *vice versa*. The relation between real co-ordinates is thus one-one, and is therefore of the form

$$axx' + bx + cx' + d = 0,$$

where  $a, b, c, d$  are constants. This argument is not valid, for we still obtain a one-one relation between the real co-ordinates if we replace  $x$  and  $x'$  by  $x^m$  and  $x'^n$  where  $m$  and  $n$  are any odd integers.

We have now to consider how to present the theory in a manner free from the objections that have been raised against the ray treatment. We shall clearly avoid these difficulties if we consider the wave as a whole and base the theory on the fundamental properties of a wave motion. In some respects the exact theory is simpler than the approximate relations used in elementary discussions; as the exact theory requires the use of mathematics somewhat too advanced for some students, we will only consider the elementary treatment here.

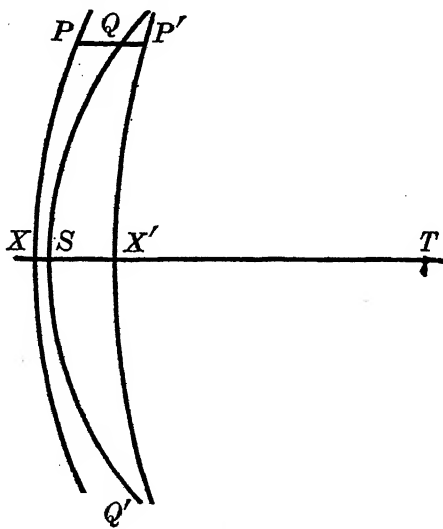


Fig. 1.

Suppose that  $QSQ'$  (Fig. 1) is a section of a refracting surface which forms part of a sphere with its centre at  $T$ . The curvature  $R$  of this surface is measured by the reciprocal of the radius  $ST$ :  $R$  is to be considered positive when the incident light passes through the surface from the convex to the concave side. Let  $PX$  represent in section a spherical incident wave, having its centre of curvature on the straight line  $XST$ , just before refraction; and similarly let  $P'X'$  represent the wave in section just after refraction. From the symmetry of the incident wave and the refracting surface about  $ST$  we can say that, if the media on either side of  $QSQ'$  are homogeneous, the emergent wave will also be symmetrical about the same axis. Thus the equations to the three surfaces may be written in the form:

Incident wave	$x = x_0 + \frac{1}{2}y^2U + \text{terms in } y^4, y^6, \dots,$
Refracting surface	$\xi = \xi_0 + \frac{1}{2}y^2R + \text{terms in } y^4, y^6, \dots,$
Emergent wave	$x' = x'_0 + \frac{1}{2}y^2V + \text{terms in } y^4, y^6, \dots,$

where  $U$  and  $V$  are the curvatures (bearing the signs of similarly oriented refracting surfaces) near the axis of the incident and emergent waves. Now the light travels along the axis from  $X$  to  $X'$  through  $S$ : let us suppose that  $PQ_1P_1'$  is the stationary path from  $P$  to the emergent wave. By the properties of a stationary path any near path will differ in length from the stationary path by a negligibly small quantity. We therefore make a negligible error by substituting  $PQP'$ , a straight line parallel to the axis, for the actual stationary path. As the time taken to go from  $P$  to  $P'$  is equal to that required by the light to travel from  $X$  to  $X'$ , we have, since the time needed to traverse a given length is proportional to the refractive index,

$$\mu.PQ + \mu'.QP' = \mu.XS + \mu'.SX',$$

$$\text{or} \quad \mu(\xi - x) + \mu'(x' - \xi') = \mu(\xi_0 - x_0) + \mu'(x'_0 - \xi_0),$$

or, since the  $y$ 's for all the surfaces are equal,

$$\frac{1}{2}y^2\{\mu(R - U) + \mu'(V - R) + \text{terms in } y^2, y^4, \dots\} = 0.$$

We assume that we commit no serious error by supposing all the surfaces to be strictly spherical. We can then neglect the terms involving  $y$  in the bracket, since the correct result is determined by the leading terms. Moreover the range for  $y$  is finite, and we thus reach the equation of refraction

$$\mu'V - \mu U = (\mu' - \mu)R = \text{constant} \quad \dots\dots(1)^*.$$

This constant is called the power of the surface. Equation (1) represents a change in the curvature of the wave which occurs as the light passes through the refracting surface. The effect is easily visualised.

If now the emergent wave encounters a second refracting surface of curvature  $S$  separating media of indices  $\mu'$  and  $\mu''$  immediately after it has passed through the first surface, the curvature of the wave on incidence at the second surface will be sensibly the same as that with which it emerged from the first surface, and the equation for the second refraction will be

$$\mu''W - \mu'V = (\mu'' - \mu')S = \text{constant}.$$

Adding this to the first equation we obtain

$$\mu''W - \mu U = (\mu' - \mu)R + (\mu'' - \mu')S = \text{constant},$$

which is essentially of the same form as (1). It follows that (1) may be at once generalised to apply to any number of refractions at surfaces crossing the axis in the immediate neighbourhood of a single axial point. Powers are merely additive. In the important case when the external media are air, for which the refractive index is assigned the value unity, the equation becomes

$$V - U = F \quad \dots\dots(2).$$

It may be observed that when light travels in the reverse direction the signs of the curvatures  $R$ ,  $U$ ,  $V$  are changed, and also the various media are encountered in the reverse order, causing an additional change of sign. It follows that the equations are independent of the direction in which the light travels.

\* The systematic treatment of lens theory by this "curvature method" was initiated by Prof. S. P. Thompson, and extended by Dr C. V. Drysdale.

Equations (1) and (2) are specially simple forms of the linear equation

$$a + b \cdot \mu U - c \cdot \mu' V - d \cdot \mu U \cdot \mu' V = 0 \quad \dots\dots(3).$$

This equation remains linear if we convert it from a relation between curvatures into a relation between lengths, viz.

$$a \cdot \frac{u}{\mu} \cdot \frac{v}{\mu'} + b \cdot \frac{v}{\mu'} - c \cdot \frac{u}{\mu} - d = 0 \quad \dots\dots(4).$$

The  $u$  and  $v$  in this equation are the distances of the centres of curvature of the incident and emergent waves from the vertex  $S$  of the refracting surface. Since we suppose that the waves are spherical, they will remain spherical, although of changing curvature, as they travel onwards. Thus when the incident wave was still a distance  $t$  from the vertex of the first refracting surface, the front was a portion of a sphere of radius  $u_1 = u + t$ , and similarly after travelling a distance  $t'$  from the vertex of the last surface the emergent wave will form a portion of a sphere of radius  $v_1 = v - t'$ . If we substitute from these equations for  $u$  and  $v$  in (4), we obtain an equation which we may write

$$a' \cdot \frac{u_1}{\mu} \cdot \frac{v_1}{\mu'} + b' \cdot \frac{v_1}{\mu'} - c' \cdot \frac{u_1}{\mu} - d' = 0 \quad \dots\dots(5),$$

where  $a', b', c', d'$  are functions of  $a, b, c, d, t/\mu, t'/\mu'$ . We may now reconvert (5) into an equation connecting the curvatures  $U_1$  and  $V_1$  of the incident and emergent waves at distances  $t$  and  $t'$  from the first and last surfaces respectively, viz.

$$a' + b' \cdot \mu U_1 - c' \cdot \mu' V_1 - d' \cdot \mu U_1 \cdot \mu' V_1 = 0 \quad \dots\dots(6).$$

In this form the equation is suitable for taking into account refractions where the wave curvatures are  $U_1$  and  $V_1$  respectively, leading to new constants  $a'', b'', c'', d''$  which depend only on  $a', b', c', d'$  and the powers of the new refractions. Obviously the process may be indefinitely extended, and equations corresponding to (5) and (6) may be found for any system of refracting surfaces symmetrical about an axis. Now  $a'', b'', c'', d''$  are constants, that is to say they are independent of the curvatures the incident and emergent waves happen to possess. It follows that the properties of the system of lenses are contained in the values of these constants, and to find these properties we only need to be able to calculate the constants. One method, but a very poor one, of obtaining them consists in finding step by step the values of the final  $V$ 's for arbitrarily selected initial  $U$ 's. I suggest that it is a mistake to lose so favourable an opportunity of introducing the pupil to simple matrices. They represent by far the least laborious method of finding the properties of the system, and their use should excite the interest of the student in a manner which is not otherwise easy when the algebra is of a rather monotonous kind. It is readily seen that when the systems  $a_1, b_1, c_1, d_1$  and  $a_2, b_2, c_2, d_2$  are combined to form the compound system  $a_{12}, b_{12}, c_{12}, d_{12}$ , the relations between these constants are

$$\begin{pmatrix} b_1 & d_1 \\ a & c_1 \end{pmatrix} \begin{pmatrix} b_2 & d_2 \\ a_2 & c_2 \end{pmatrix} = \begin{pmatrix} b_{12} & d_{12} \\ a_{12} & c_{12} \end{pmatrix} \quad \dots\dots(7).$$

Of the four components of any matrix,  $b$  and  $c$  are pure numbers,  $a$  is a power, and



$d$  is a length—Cotes' "apparent distance" with its sign changed. Thus for a thin lens or a single surface the matrix is

$$\begin{pmatrix} 1 & 0 \\ a & 1 \end{pmatrix},$$

and for a displacement of the point where the wave curvature is measured through the non-virtual distance  $t$  the matrix is

$$\begin{pmatrix} 1 & -t/\mu \\ 0 & 1 \end{pmatrix}$$

Thus the four constants of a single lens of refractive index  $\mu$  and axial thickness  $t$ , with surfaces of curvatures  $R$  and  $S$  respectively, are given by the product

$$\begin{pmatrix} 1 & 0 \\ R(\mu - 1) & 1 \end{pmatrix} \begin{pmatrix} 1 & -t/\mu \\ 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ S(1 - \mu) & 1 \end{pmatrix},$$

the lens being surrounded by air. By inspection of the elementary factors of the general matrix we see that

$$\begin{vmatrix} b & d \\ a & c \end{vmatrix} = 1.$$

We may modify the generalised equation for the curvatures of the wave surfaces by writing  $X$  and  $X'$  for  $U$  and  $V$  respectively. The preferred form for the equation is

$$(\mu X \quad 1) \begin{pmatrix} b & d \\ a & c \end{pmatrix} \begin{pmatrix} 1 \\ -\mu' X' \end{pmatrix} = 0,$$

and this is always valid unless  $X$  and  $X'$  are large, corresponding to considerable shrinkage of the wave front. Now according to the wave theory there is no such thing as a point image, so that there is some objection to transforming this into an expression for the distances  $x$  and  $x'$  of object and image from the external reference points for which the central matrix is constructed. So long however as we exclude all but spherical waves, symmetry entitles us to claim the centre of curvature as a mean point about which the image will be formed. With this understanding we obtain the relation which is most useful in practical work, viz.

$$(1 \quad x/\mu) \begin{pmatrix} b & d \\ a & c \end{pmatrix} \begin{pmatrix} -x'/\mu' \\ 1 \end{pmatrix} = 0.$$

We have so far only considered a wave which meets each refracting surface normally at its vertex, but we can see at once that the equations are unaltered for waves making a small angle with the refracting surface at the vertex. From symmetry the relations satisfied by such waves on refraction are independent of the sign of the small angle, and the relation is thus stationary as the angle passes through the value zero. It follows that the difference between the relation for small angles and that which we have already considered is insignificant. The same conclusion may be reached by noting that each separate refracting surface is symmetrical about its centre.

To complete our theory we require equations to show the relative distances of an object and its image from the axis of symmetry. From the symmetry of a single spherical surface about its centre we readily derive the relation

$$\frac{y}{y'} = \frac{x-r}{x'-r} = \frac{X'(R-X)}{X(R-X')} = \frac{\mu'X'}{\mu X}.$$

It is easy to generalise this in the form

$$a = \mu X (-b + 1/m) = \mu' X' (c - m),$$

where  $m$  is the transverse linear magnification  $y'/y$ .

The process we have followed of first forming equations from the physical principles of the subject, and subsequently separating the variable physical quantities—in this case the curvatures of the waves as they pass through specified points—from the constants of the system, and calculating the latter from the constructional data of the instrument, is of wide application. The student should realise the importance of following this plan wherever possible.

The familiar expressions for the positions of conjugate points relative to the cardinal points of the system are easily found if they are required. In practice nothing is gained by so doing. The positions of conjugate points with respect to the external surfaces of the system is the factor which determines the utility of the instrument. In laboratory measurements it should be obvious that greater accuracy is possible when measurements are made from the vertices of rigid surfaces than when they start from points, of which at least one is almost invariably inaccessible, that have to be located by means of their theoretical properties.

We may stop a moment to consider the expression of this class which occurs most commonly in elementary text-books. When the two reference points are conjugate to one another the apparent distance of one from the other vanishes, or  $d = 0$ . The equation connecting the curvatures (assuming the system to be immersed in air)

$$a + bU - cV = 0$$

is obviously preferable to that connecting distances, which may be written

$$a + \frac{b}{u} - \frac{c}{v} = 0.$$

Whatever conjugate points are chosen we have  $bc = 1$ , and if the unit points are selected the values are  $b = c = 1$ . The two equations then become

$$V - U = a \quad \text{.....(8)}$$

and

$$\frac{1}{v} - \frac{1}{u} = a.$$

If we compare these with the equation mentioned at the beginning of this address, we may note that the physical significance of the equation is obscured by the use of distances instead of curvatures; that by adopting the focal length as the fundamental constant instead of the power useless arithmetical operations become necessary,

and the extremely simple law for combining lenses in contact is replaced by one which precludes reliable mental estimates of the properties of the joint system; and that, by measuring distances in opposite directions on the two sides of the lens, an unnecessary and undesirable departure has been made from the practice which mathematical experience has proved to be desirable. In consequence of this change of sign the meaning of the simpler equation, that a lens increases the curvature of a wave by a constant amount, would not be evident if curvatures were used instead of distances. It is much to be desired that this particular equation should be no longer used: it should invariably be replaced by equation (8), with the dioptrie (or dioptre) as the unit of curvature and of power. The signs for powers universally employed in ophthalmic optics—plus for a converging lens, minus for a diverging lens—should be adopted.

After the student has become acquainted with the laws of optical instruments he should be shown how to prove that the apparent brightness of an extended object cannot be increased by optical means. The fact itself can with advantage be mentioned earlier in the course. For example he should be told to notice that the moon looks no brighter when seen through a telescope than when viewed by the naked eye: on the other hand a telescope greatly extends the number of stars that are visible.

I have already indicated that there is little or nothing to be gained by retaining the so-called cardinal points as those to which all measurements must be referred. Associated with these points are corresponding planes—focal planes and unit planes—the chief function of which is to facilitate graphical constructions for the paths of rays refracted through the system. It goes almost without saying that if we have to abandon the ray concept in teaching optics we shall have little use for these surfaces. But that is not the only reason for thinking there would be a definite gain in rejecting them. The teaching now given is not content with saying that there are focal surfaces and unit surfaces; it goes on to assert that these surfaces are planes, i.e. that their curvature is zero. Now the slightest consideration shows that this is not true. When the optical system consists of a single surface it is obvious that both unit surfaces coincide with the refracting surface itself: that is to say their curvature is greater than the power of the system itself. Again if we take a plano-convex or a plano-concave lens, the unit surface on the one side coincides with the curved surface, and on the other it is the image of this curved surface in the plane. Both curvatures are large, and they are unequal. We may assert as a general proposition that the surfaces are decidedly curved. The doctrine of the planes has done much, I think, to conceal the interest which should be taken in optical systems, and in particular to prevent proper appreciation of the very notable achievements which have to be placed to the credit of lens designers in recent years. I must content myself here with pointing out that the focal surface for light refracted in the vicinity of a given point on the surface of a sphere is spherical, and that as we move the point along the surface the spherical image locus moves. It is at once evident that there is enormous aberration in the image when the aperture is large, and that the task of bringing all these loci into coincidence to secure good definition, and meeting

the additional condition that this common locus, contrary to all the inclinations of the constituent lenses, is to be plane and not spherical, is one that demands great knowledge, patience, and skill. If the real facts were more fully realised, we should be as ready to recognise in the finest high-power microscope objectives and in the best rapid wide-angle photographic lenses the consummate skill of the designer, as we are to appreciate in the largest telescope discs the triumphs of the glass-maker.

I have given some indication, I fear very sketchily and imperfectly, of the way in which I think we could advantageously change the elementary teaching of optics. If anyone doubts the advantages of using matrices in optics I would suggest for his consideration the problem of an assemblage of astigmatic surfaces with their powers, their orientations, and their separations arranged haphazard. The matrix solution is of the simple form

$$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ \psi_1 & \pi_1 & 1 & 0 \\ \pi_1 & \phi_1 & 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & 0 & -\tau_1 & 0 \\ 0 & 1 & 0 & -\tau_1 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ \psi_2 & \pi_2 & 1 & 0 \\ \pi_2 & \phi_2 & 0 & 1 \end{pmatrix} \dots\dots,$$

where  $\phi$ ,  $\psi$ ,  $\pi$  are the component powers at a single surface, and the separations between successive surfaces are represented by  $\mu\tau$ . The gain secured by separating the wave curvatures from the constructional particulars of the system becomes more pronounced as the system grows in complexity. The discovery of an optical system to satisfy given conditions reduces itself to the routine solution of a matrix equation.

Space will not permit me to deal in detail with more advanced instruction. I would merely express my conviction that the line of progress lies in the application of Hamilton's methods to these problems. We effect a great simplification at the very beginning. We need not consider the form of the light-waves at all; the fact that they are absent from our fundamental matrix equations shows that they are not in fact pertinent to the problem. In Hamilton's methods such superfluous quantities are not introduced.

On the experimental side I have some ground for thinking that there is a widespread failure in places of higher education to realise what is reasonable accuracy in ordinary optical experiments. The special technique of the most refined measurements is a quite distinct matter, and does not fall within the province of educational institutions. To take a simple example it should be realised that for ordinary industrial purposes the refractive index of a glass is unknown unless its value is obtained to within two or three units of the fourth decimal place; the dispersion should be known to the same number of units in the fifth place. Greater attention should be devoted to the significance of the exact procedure followed in experimental observations. Accuracy of focussing for instance should be judged by sharpness, not by parallax. I suggest that some consideration should be given to the value, for instructional purposes, of a general utility interferometer. It does not appear to me that the cost of an efficient instrument would necessarily prove the decisive factor.

## 2. SUGGESTIONS RELATING TO REFORM IN THE TEACHING OF GEOMETRICAL OPTICS

By C. W. HANSEL, Bedford School

*ABSTRACT.* Reform in teaching will only come through pressure brought to bear by examinations. Experimental work should be devised in which the student must exercise his originality and resource in devising his apparatus and methods. The student should be given far more opportunity of making himself familiar with the construction and performance of optical instruments. Graphical exercises could be devised to supplement the experimental work. An appeal is made to mathematicians to state their problems wherever possible in non-mathematical language.

THE type of training provided by our schools is largely adapted to suit the requirements of examinations. For this reason it may be said that examining bodies are almost entirely responsible not only for the subject-matter of what is taught but also for the method of teaching it. Any reform in the teaching of geometrical optics in schools can only come by modification of the syllabuses of the examinations for scholarships, university entrance, and school leaving examinations with simultaneous modification in the view-point of the examiners. Teachers, text-book writers, courses of practical work, and the equipment of school laboratories, will all adjust themselves to new circumstances and new ideas in order to conform to examination requirements; but reform, even if obviously urgent and desirable, will never come into the schools unless it is encouraged through the avenue of examinations.

To influence examining bodies to the extent of introducing fundamental changes of syllabus, will require very definite proposals of compelling urgency and with obvious educational advantages. Such a scheme can only be formulated by close and expert collaboration between teachers and industrialists. Men of knowledge and experience must cooperate sympathetically and must be given suitable facilities so that contact may be established between educational and industrial points of view. Sufficient time and labour must be devoted to the problem to allow of a thorough exchange of views. Any scheme formulated must take into account existing conditions and must provide some guidance for examiners and teachers. A report carefully drawn up and explaining the scheme, together with suggestions and exercises, could probably be published so as to be available at small cost.

It is possible that present methods of teaching may be too academic and non-technical. More attention might be given to industrial processes, e.g. optical glass, silvering, polishing, etc. Photometric work might be brought more into line with industrial requirements. More attention might be devoted to the construction and performance of optical instruments, the defects of optical systems and their cor-

rection, optical tests, etc. It is suggested that the methods employed in teaching geometrical optics are unsuitable and useless for dealing with industrial problems. It must be remembered, however, that beginners have a very meagre range of mathematical equipment, and that the majority of those in schools will never pursue their optical studies for industrial ends.

The most important part of the work should be the laboratory work. There seems to be a general tendency to regard practical work in optics as a series of experiments in which refractive indices, focal lengths, magnifying powers, etc. are measured in as many different ways as possible. A sufficient number of pin, parallax, and screen experiments would seem to provide the elementary student with the necessary optical training. Much that is useful can be done by such a course if it is suitably enlarged with graphical and numerical exercises, but there is danger of this work becoming a mere mechanical examination, routine. Too often the student is supplied with apparatus which suggests or even prescribes for him his method of experimenting and leaves nothing to his originality or resource. It is highly desirable that the student should exercise himself on the design of his apparatus and in devising satisfactory means for the solution of his problem. In the interests of economy, apparatus must be inexpensive but adaptable, and it should be capable of easy and universal adjustment in so far as this is required.

Perhaps the most important defect of present-day teaching is that it fails to supply a sufficient practical acquaintance with optical instruments and their performance. Many students of optics use telescopes and microscopes and they are given a simple theory of these instruments. Too often, they are quite unfamiliar with the construction of an eyepiece, the position and function of the lenses and stops in an instrument, questions relating to suitable illumination, etc. The construction of optical apparatus and instruments is a part of the practical training which is most seriously neglected. Apparatus and instruments should be capable of assembly in more than one way, and the discovery of the best method of construction and arrangement, and a criticism of inferior designs, is an essential and valuable part of any course of practical training. Those engaged in the optical industries would render valuable service if they would furnish some simple examples of preliminary exercises, numerical and practical, forming a suitable introduction to the design of optical instruments. Also, they could indicate some important tests, such as the Hartmann test, which might be modified suitably to enable them to be carried out effectively with simple apparatus.

The following apparatus is suitable for beginners. Let a number of parallel lines be ruled on an ordinary blackened lantern slide about  $\frac{3}{16}$  in. apart. Let the slide be fixed in a vertical position with a bright flash lamp behind it and a cylindrical lens in front of it. By adjusting the position of the lamp, it is possible to project a parallel, convergent, or divergent beam of light on a white card placed in front of the slide. A second cylindrical lens may be placed in the path of the beam, and a test made of its spherical aberration. The chromatic aberration may be dealt with, using coloured glasses. The path of a ray through various optical elements may be exhibited by the use of a black slide with one or more slits.

Some brief reference may be made to elementary numerical and graphical work. In dealing with simple problems on axial pencils, I have found the following method simple and effective.

The figure shows the ordinary method of finding the position of the image formed by a thin convex lens where the position of the object is given. By rotation of the line  $PQ$  about  $O$  its intersections with  $m = 1$  and the line  $QF$  give corresponding positions of object and image respectively.

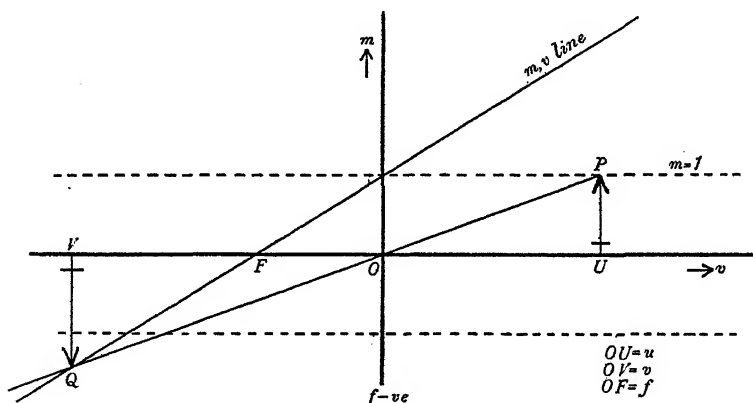
For a thin convex lens the magnification  $m$  is given by

$$m = -\frac{v}{f} + 1.$$

Thus the line  $QF$  is also the line obtained by plotting  $m$  against  $v$ .

The same diagram may be used to give a geometrical proof of the lens formula.

The magnifying power of the lens is the ordinate to the  $m, v$  line for  $v = d$ , where  $d$  is the nearest distance of distinct vision.



The method is quite general and may be applied to axial pencils through any optical system consisting of reflecting or refracting surfaces.

By the previous method the numerical and graphical treatment may be combined.

A graphical construction which I have found very useful in many problems (caustic curves, theory of rainbow, thick lenses, etc.) is given in Drude's *Optics*\*, and stated to be the "method of Weierstrass." It was given by Thomas Young in 1807 and by Weierstrass in 1858.

Attention may also be directed to a paper on graphical methods by Mr J. H. Dowell†. The methods here given are simple, elegant, and of wide generality. They are capable of numerical interpretation with the use of simple mathematics. Much valuable work could be done, by the methods described in this paper, with a large drawing-board, compasses, and parallel rule (or set squares).

\* Drude, *Optics*, English translation, p. 32.

† J. H. Dowell, *Proceedings of the Optical Convention*, p. 965 (1926).

The *Proceedings of the Optical Convention* and the *Dictionary of Applied Physics* contain a mass of valuable information on optical problems. Much of this work carries little conviction to non-mathematical readers owing to the principles involved being totally obscured by a mass of mathematical symbols. The writer is of the opinion that many of these very valuable articles would make a much wider appeal if the mathematical results were stated alternatively in simple language and given a definite physical interpretation whenever this is possible. As examples of non-mathematical exposition of the kind advocated mention may be made of the papers contributed to the *Proceedings of the Optical Convention* 1926 by Miss H. G. Conrady\* and Mr R. Kingslake†.

\* Miss H. G. Conrady, "Spherical Aberration on Optical Images," *Proc. Optical Convention*, p. 830 (1926).

† R. Kingslake, "Developments of the Hartmann Test," *Proc. Optical Convention*, p. 839 (1926).



### 3. THE PRESENT SCHOOL CERTIFICATE COURSE IN OPTICS

By S. R. HUMBY, M.A., The College, Winchester

*ABSTRACT.* Many pupils after taking the usual first school course in Optics are found to have learnt little more than a geometrical construction and an algebraic formula. Emphasis should be placed on the artificial nature of the conventional treatment as well as on its usefulness. A course of very simple practical work, carefully designed to illustrate how optical instruments behave and how light passes through them, should provide this emphasis.

THERE still seems to be a strong tendency to regard the early course in optics as almost entirely a drill in geometrical diagrams and in elementary algebra. It is, incidentally, a matter of interest that the reciprocal equations are very difficult to many boys chiefly, it would seem, through lack of earlier practice in mental arithmetic and the conversion of simple fractions into decimals and decimals into their nearest simple fractions.

This treatment of elementary optics from a geometrical rather than from a physical point of view is of course partly due to the syllabus and to the type of question set in the First School Examinations.

It is comparatively easy for an examiner to set a variety of numerical examples on lenses or mirrors, and such questions are so much easier to mark rapidly and fairly that they are sure to hold an important position in the examinations and therefore in the teaching of the subject. As a result the writer has found that comparatively few of the abler candidates attempt the more qualitative questions on physical optics while the smaller allowance of time given to the other parts of the subject leave the weaker candidates hopelessly vague about them.

In School Certificate Examination scripts the answers show much confusion about the simple geometrical method of locating an image by a diagram. Many candidates have apparently never realised that the essential condition for a good lens or mirror is that all rays which strike it from a point on the object shall pass through a point image. It is evidently very necessary for us to emphasise the artificial nature of the conventional diagram as well as its great use.

The position in space of an image is another thing about which ideas are usually very vague. The writer, from his own experience, finds it best to begin by pointing out the two possible ways of fixing the position of a ghost by offering it a chair (if friendly) or by taking bearings on it from suitable positions. The location of images from mirrors, lenses and more complicated instruments can then be referred to these two possible methods.

In answers to questions which require the tracing of a pencil of rays through a system from a point on the object to the eye most candidates (and some text-

books) just give two geometrical diagrams for locating the image. It is evident that the pupils have never been made to realise that a ray of light which suddenly and abruptly changes its direction at a point in space is a most unnatural phenomenon. The trouble is mainly due, no doubt, to the difficulty of making clear diagrams in which the angles subtended by objects are reasonably small.

It seems that it is very necessary to provide practice in drawing approximate paths of rays which strike mirrors and lenses in directions other than the two or three standard ones. Very simple apparatus can be made to show these paths and those students who perform, or are shown repeatedly, simple experiments with rays of light are more likely to realise something of the relative amounts of light which pass into and are reflected back from a refracting surface. They will therefore recognise total internal reflection as a natural phenomenon rather than an apparently arbitrary mathematical relation.

In practical work the writer finds that much confusion is produced in the most elementary stages by the practice of finding focal lengths by four or five different methods, probably on different days. The pupils not unnaturally get the idea that these methods are arbitrary devices to defeat examiners. Perhaps the best way out of this difficulty is to insist on an approximate direct measurement of focal length by the distant object method each time before a new method is attempted. It seems also necessary to give a good deal of practice with real images caught on screens before attempting the much more difficult pin methods.

It is curious that unit magnification methods are so rarely described in elementary text-books for conditions where image and object can be made to coincide. Their equality in size is at once evident and, with beginners, adjustment for equality in length is a matter of seconds whereas the no-parallax position for a pin is very difficult to find.

#### 4. REMARKS ON THE TEACHING OF GEOMETRICAL OPTICS TO ELEMENTARY STUDENTS

By H. H. EMSLEY

*ABSTRACT.* It is suggested that the teaching of the earlier stages of geometrical optics from the experimental point of view, the introduction of mathematics being postponed until later, would benefit larger numbers of students and at the same time provide those who are to pass on to more advanced work with a useful practical groundwork. In deciding upon a system of nomenclature and conventions, consideration should again be given to non-mathematical students and to the conventions established in the ophthalmic industry.

I REGRET that pressure of work has prevented me from joining very actively in what is undoubtedly a discussion of great importance to all interested in the teaching of optics. The points I am able to advance concern only the elementary portions of the subject of geometrical optics and amount practically to a plea that, in any scheme that may be formulated as a result of this discussion, consideration be shown to the non-mathematical student in general and to the large number of students of ophthalmic optics in particular.

Useful work in the adjusting, testing and using of optical appliances and even in the designing of many optical systems can undoubtedly be carried out by people equipped with little mathematics; and the teaching of geometrical optics in its earlier stages would benefit larger numbers of students if the subject were presented from the experimental rather than from the mathematical point of view. At present there is a wide gap between courses of study or text-books concerned merely with the simple elements of paraxial image formation, etc. (designed only too often merely to train for examinations and almost useless in practice) and courses or text-books on geometrical theory in which the whole presentation is supported on a mathematical framework which the non-mathematical student is unable to comprehend, although he may be quite capable on the experimental side and sound in his grasp of the physical nature of the problems involved.

I would suggest that the subject should be presented experimentally until the higher branches are reached. The students are learning mathematics simultaneously and those who are to proceed with the higher branches of geometrical theory will benefit by their early training on the experimental and practical side. In the elementary portions too, the paraxial (Gaussian) image formation should be developed as a special case after a certain amount of work has been done in tracing wide aperture rays and waves through surfaces and lenses, graphically, trigonometrically and experimentally, as is the case when dealing with prisms. For the experiments a large lens of about 10 or 12 in. aperture, capable of rotation about a vertical axis which may be in or beyond the plane of the lens, is extremely useful

in giving the student an idea of the meaning of chromatic and spherical aberration, coma, astigmatism, etc., diaphragms with small circular and annular apertures in various zones being used with the lens.

Although I would not advocate a rigid adherence to the curvature method of teaching geometrical optics, yet the method is helpful to the elementary student and can be usefully introduced alongside the ray method, capital letters being used to designate curvatures and powers and length reciprocals generally (see below).

The prismatic action of lenses should be presented. Experiments on the astigmatic image formation by sphero-cylindrical lenses could with advantage be introduced at an early stage, to give point to the meaning of stigmatic or homocentric image formation assumed in the geometrical theory when dealing with spherical surfaces.

Elementary ideas on interference and diffraction and the resolving power, numerical aperture, etc., of instruments might be incorporated much earlier than is usual.

The first ten chapters of Müller-Pouillet's section on optics, simplified for the beginner and supplemented by experimental, workshop and graphical work, seems to me to provide a useful guide in formulating a course on elementary geometrical optics, intended equally for those students who need to go no farther and for those who are to specialise on higher work in optics.

Great benefit would result from a few periods in the lens workshop devoted to the working and polishing of a simple lens surface on glass the refractive index of which has been measured by the students, the finished lens being measured for focal length on the optical bench.

The question of nomenclature and conventions as to signs, etc., is of minor interest in this discussion, I understand; nevertheless, having in mind the large numbers of ophthalmic students and the by no means negligible effect they will have on the optical industry, I would urge that any system of nomenclature that may be recommended should take into account the conventions that have become firmly established in the ophthalmic industry and the methods that have proved satisfactory in teaching students of ophthalmic optics. The main points may be summarised thus:

(1) A converging system has a positive focal length measured from the system to the second focal point. This fixes the direction of the incident light as the positive direction.

It should be an easy matter to fit this requirement into a wider and more rigorous scheme required by students of the higher branches of the subject\*.

(2) The usual convention as to signs taught in schools should be adopted; distances to the right of and upwards from the point of reference to be positive, and (a point of less importance) counterclockwise rotations to be positive.

The incident light would therefore be taken usually as from left to right.

This would obviate the need for unlearning the notion of signs acquired by the elementary student in his school work, besides being practical.

\* Müller-Pouillet, 3rd ed., chap. 3.

(3) Capital letters should be reserved for quantities the dimensions of which are  $L^{-1}$ —curvatures, vergencies, powers of systems, etc. To avoid confusion these capitals could be in script form as distinct from the block capitals used for other purposes. Whether the curvature method of teaching geometrical optics be used or not, the use of separate symbols for reciprocals of lengths such as curvatures and focal powers is undoubtedly helpful to the elementary student. It was urged by the late Mr Chalmers.

Thus the power of a system (in air) of focal length  $f$  is denoted by  $F$  (or  $\mathcal{F}$ ); the curvature of the wave-front of light incident from a distance  $u$  is represented by  $U$  (or  $\mathcal{U}$ ); the curvature of a surface of radius  $r$  by  $R$  (or  $\mathcal{R}$ ), etc.

These three underlying conventions are already in use at the Northampton Institute and, I believe, with one or two minor exceptions, at the Imperial College of Science. The symbols used at the former institution in designating the more important points, distances, etc. have recently been published in another place.

## 5. GEOMETRICAL OPTICS AT THE CAVENDISH LABORATORY

BY DR G. F. C. SEARLE, F.R.S., University Lecturer in Experimental  
Physics, Cambridge

*ABSTRACT.* The paper is based on experience with a practical class at the Cavendish Laboratory. Many students show little care for accuracy. They are encouraged to attempt accurate measurements: this arouses their interest. The optical parts supplied to students should be of good quality. Students should be encouraged to use a magnifying glass in making accurate settings. The convention of signs adopted is that which makes all signs positive in the formula for a converging lens. Thick lenses and lens systems are taken at an early stage in the course.

I AM not qualified to speak of the teaching of geometrical optics generally, for my limited experience has been gained in my own practical class at the Cavendish Laboratory, and in that work I have had little occasion to teach more than the elements of the geometrical theory.

At Cambridge, geometrical optics has a small place in Part I of the Mathematical Tripos, but the questions can be answered without any practical acquaintance with the subject and not many of those who teach for that Tripos have themselves any practical knowledge of optical work.

Optics was removed from Schedule A of Part II (the advanced part) of the Mathematical Tripos some years ago on the ground, I believe, that it was not intellectually interesting, and thermodynamics was put in its place. The effect, of course, has been to diminish the number of serious mathematicians who know anything about optics and to deprive teachers of the opportunity of teaching the subject.

Some years ago Mr T. G. Bedford and I gave some experimental lectures on geometrical optics for candidates for Part I of the Mathematical Tripos. We did not attempt a mathematical treatment but merely endeavoured to show the simpler phenomena on a bold scale and to indicate how measurements can be made. The students were obviously interested, but the lectures were discontinued after the second year because pressure on the lecture-room accommodation prevented us from arranging the experiments.

At the Cavendish Laboratory, both geometrical and physical optics, to use a common distinction, are taught to students preparing for Part I of the Natural Sciences Tripos. The practical work in geometrical optics includes experiments on mirrors, prisms and lenses; the range of work may be seen in my *Experimental Optics*.

In Part II of the Natural Sciences Tripos, the optics is "physical" and there is no insistence on geometrical optics.

The teaching for Part I of the Natural Sciences Tripos is intended more as a

part of a general education than as providing a specialised training in any one subject, and thus, if we can impart a sound knowledge of the fundamental principles of geometrical optics and can teach students how to do accurate and methodical work in experiments which interest them, we have fairly fulfilled the duty allotted to us.

In a course of lectures on geometrical optics, the lecturer is free to select a number of propositions and to arrange them in the best possible way. But, in a practical class, the experiments are determined by the apparatus which the teacher has at his disposal. Thus, experiments on the variation of refractive index with wave-length may have to wait until a mercury arc lamp is available. Since only a limited number of experiments can be done in one term, the more exciting experiments are apt to crowd out the less exciting. This process is often aided by the students who have, many of them, become blasé after several years of school physics. If an experiment buzzes or stands on its head or is otherwise thrilling, students will clamour for it, though they may understand little of the principles involved. For this reason experiments on geometrical optics are in danger of being left on one side.

In my own class we have to deal with students who have done physics for as many as five or six years in some cases. Many have never been taught to care for accuracy and are content to continue in their old way. The majority are quite happy in focussing a telescope on a distant object through dirty crinkly window glass, and only a few have any idea how to find an approximate value of the focal length of a converging lens by observing the image of the sun. Many take little care in placing the object point on the axis of the lens. They are awarded the O.N.E.—the Order of the Near Enough.

Oh, let me be dismal and work in the dark  
With lenses all crooked and dim,

seems to express their outlook.

We do our best to cure this state of things and our efforts meet with fair success. I think that the cause of the trouble is that the students have not been sufficiently encouraged to attempt accurate measurements. Geometrical optics, done anyhow, is very dull. When, however, the experiment is hard enough to call forth a real effort, the student "gets his blood up" and finds interest and pleasure in the work. One student told me that he took no interest in optics till I made him work accurately.

I am fully aware that the geometrical optics taught in my class would need much development if the training of practical opticians were in view. But to teach students to recognise small differences in the quality of images and to lead them to appreciate the importance of accuracy in aligning lenses is not generally possible when one teacher is expected to teach about fifteen students and when, as sometimes happens in universities, the junior teachers have little more experience than the students. I do not know that much encouragement is given to teachers to make themselves proficient. If a young man is engaged on Research, he is a Pioneer and a Hero, but if he teaches—well, he is just a teacher.

I would make an earnest plea that the optical parts supplied to students should be of good quality. Teachers should not be content to provide a piece of shiny material that is not obviously uneven for use as a plane mirror. It will not be possible to provide optical flats for students, but if pieces of stout mirror glass are selected by aid of a telescope, students are unlikely to meet with any difficulty arising from the imperfection of the mirror. If possible, students and laboratory assistants should be taught how to test a plate against the face of a good plate or prism by means of Newton's rings.

My eyes have for some years lost so much power of accommodation that I have forgotten what it is like to see images with the eyes of a young man and I have to use a magnifying lens in cases where 40 years ago I should not have needed its aid. But I feel sure that students should be taught at an early stage to use a magnifying lens in making optical settings in order that they may get the stimulus which comes from an endeavour to work accurately.

We often find that a student will focus an eyepiece so that the image of the cross-wires formed by the eyepiece is not at infinity but is perhaps not more than 10 cm. from his eye, although his vision for distant objects is not in the least defective. It is useless to expect such a student to use a microscope or a telescope to determine the position of an object by adjusting the microscope or telescope along an optical bench, unless the instrument be provided with cross-wires or with a micrometer scale which may be used in the parallax test.

Some students stare at an image for a long time before passing any judgment on its position. This spoils their vision and leads to gross errors. I have known an able student make errors of 10 or 20 cm. on an optical bench in experiments where a normal person would not be wrong by  $\frac{1}{2}$  cm. unless he were very careless. Such students need to learn to come to a speedy decision.

Some students have not learned to focus accurately. They will work with a spectrometer and a grating capable of giving a very obvious resolution of the *D* lines of sodium and will not see the lines separate until the teacher helps them. On the other hand, when the laboratory possesses good spectrometers, the teacher is always pleased to hear a student ask what is the purpose of the vertical wire down the centre of the slit, for then he knows that the student has, unawares, discovered the separation of the *D* lines for himself.

In one respect I have departed from some text books. I call the focal length of a converging lens positive and, when the real object and its image are on opposite sides of the lens, I call both *u* and *v* positive, so that the equation becomes

$$1/u + 1/v = 1/f.$$

I believe I have been blamed for this although I have several respectable authorities on my side.

When the object is a flame or other luminous source and the image is received on a screen, there may be some point in measuring both distances "towards the light." But when the object is one pin point and a second pin point is set on the image of the first, there seems no reason for taking one direction as positive rather



than the other. It is therefore more natural and more simple to measure the distance of the object from the lens in one direction and the distance of the image in the opposite direction and thus gain the benefit of a symmetrical notation for a symmetrical arrangement.

As regards taking the focal length of a converging lens as positive, this is exactly what is done by practical opticians.

When a person skilled in optical calculations has to deal with a system of many lenses, he may find it more convenient to measure all distances in the same direction. He will escape disaster because he is skilled and will not make mistakes as to the signs of the quantities. But, when an ordinary person has to deal with a simple lens, he does best to adopt the simplest method and that method is the symmetrical method. My experience leads me to think that among unskilled persons those who make the most conventions make the most mistakes. Some years ago a physicist told me that he never could tell by calculation on which side of a lens the image is, and I had no reason to doubt his word.

I am not sure that the "teaching of geometrical optics" amounts to much more than talking about the eternal question as to whether to write  $1/u + 1/v$  or  $1/u - 1/v$ . To have to decide this point is for many a worse trial than the attempt to find out when the twentieth century began.

An examination of the books in which the focal length of a converging lens is taken as negative and distances are measured "towards the light," and a consideration of the explanations given to make it all perfectly simple, will convince the candid reader that there is something wrong.

When a student arrives in my class with his mind entirely fogged as to sign conventions, I teach him the deviation method of treating thin lenses and then his difficulties, as a rule, disappear. All he needs to remember is that, if a ray in a plane containing the axis meet a thin lens at distance  $h$  from the axis, the direction of the ray is changed by  $h/f$  in passing through the lens.

We do not treat a thin lens as the standard form of lens and then consider it a hardship to be compelled to treat some lenses as thick, but we begin at an early stage with thick lenses or systems of lenses, using exact formulae. When the fundamental theorems are approached by way of Helmholtz's formula they present little difficulty to students.

I feel sure that much of the confusion over  $1/u + 1/v$  and  $1/u - 1/v$  arises from a failure to distinguish between the algebraical sign prefixed to a symbol in an equation and the positive or negative character of the numerical value which is assigned to the symbol when an actual numerical computation has to be made. This trouble is not likely to distress students who have already a sound knowledge of the fundamentals of algebra and are sure of what they do with symbols. But many who do optical experiments have not got that sound knowledge. They can do algebra up to a point and no doubt would suspect an error if the number of bulls came out to be " $-14.027$ ," though they might explain the negative sign as indicating cows. But when in optics they find by calculation that the image is 17 cm. from the lens on the same side as the object there is nothing to warn them that they are wrong

unless they make an experimental test or follow the advice of some text books and verify their calculation by aid of a graphical construction. Systems of calculation which need graphical confirmation stand self-condemned.

Optics suffers from a special disadvantage which limits the appreciation of the science by non-technical teachers and students. An image of sorts can be obtained with a lens which is not "corrected" for the purpose in hand and with very poor setting, and this image is sufficiently good to satisfy many. It is difficult to excite their interest in the technical skill involved in the design of lenses to fulfil definite conditions, in the methods of constructing lenses or in the art of producing the optical glasses of which the lenses are made. Few have ever seen the grinding of lenses or the figuring of prisms or mirrors, and fewer still have done these things with their own hands, and thus their lack of appreciation of the work of technical opticians is only natural. Besides all this, optics is an old science and therefore does not appeal to those who hope to make names for themselves in the latest developments, probably ephemeral, of physics.

Those, if any there be, who look to me to give a prescription for putting geometrical optics into a better position will be disappointed. The elements of the subject are simple and are easily taught, but their applications to practical optics, when fully developed, are far from simple, as may be gathered from such a book as the *Principles and Methods of Geometrical Optics*, by James P. C. Southall, or from any book on lens design. It is therefore not to be expected that there will ever be many who are expert on the theoretical side.

If each teacher presents geometrical optics in a convincing and interesting way within the limitations under which he works, this is perhaps as much as teachers can do for the subject at present. Greater prosperity in the optical trade would provide opportunities for the development of the subject, but this aspect of the matter is outside my province.

## 6. THE TEACHING OF OPTICS BY THE WAVE OR CURVATURE METHOD

By C. V. DRYSDALE, O.B.E., D.Sc., F.R.S.E.

**ABSTRACT.** The teaching of optics by the wave or curvature method is advocated on the grounds that it (a) simplifies elementary teaching, (b) harmonises the teaching of science students and opticians, and (c) leads naturally to higher physical optics. A large number of opticians present themselves annually for examinations, and the majority of them find it difficult to obtain suitable instruction, as the trade nomenclature is based on the curvature system. Although it is generally known that wave methods can be employed for elementary teaching, there seems to be an impression that they must be abandoned for the study of aberrations and optical design, and that it is therefore better to start with geometrical methods at the outset; but this is a mistake. The first order aberrations can be more easily dealt with by the curvature treatment, and the results harmonise completely with the indications of the lens testing interferometer. The paper contains a sketch of a systematic course on optics, including the Gauss theory and the treatment of aberrations, in which wave methods are employed.

### § 1. INTRODUCTION

ALTHOUGH it is fairly generally known that the whole of elementary optical theory can be taught by the wave or curvature method, and with considerable simplification in many parts of the subject, few teachers appear to have adopted it, and probably the late Prof. Silvanus Thompson\* and the present writer are alone in having employed it systematically.

To some extent this may be due to the lack of a complete text-book on the subject, but there seems to be a general impression that the wave method is unsuitable for the treatment of aberrations, and that since the geometrical or ray method must be employed for this purpose it is better to adopt it from the outset. This impression is however incorrect, and in the writer's optical lectures at the Northampton Institute, not only was the wave method used for the whole of elementary optics, but it was carried on to the teaching of aberrations and the design of lens systems. An outline of the elementary course was given to the Physical Society in 1905†, and a fairly complete exposition of it in a series of articles in the *British Optical Journal*‡, but no publication of the application to aberrations was made until the Traill Taylor lecture before the Royal Photographic Society last year§.

\* "Notes on Geometrical Optics," S. P. Thompson, *Phil. Mag.* 33 (1), 232-248 (1889).

† "On the Curvature Method of Teaching Optics," *Proc. Phys. Soc.* 19 (1905). *Phil. Mag.* April (1905).

‡ "Applied Optics," *British Optical Journal*, (1901-3).

§ *The Photographic Journal*, March, April, and May (1928).

The advantages of the wave method of teaching may be stated as follows:

1. Elementary optics is considerably simplified, as trigonometrical formulae and approximations are very rarely required. Signs and conventions are also simplified.
2. The gap between scientific optics and spectacle optics is removed.
3. It puts the whole of optical teaching on a physical basis, and leads naturally to the study of interference, diffraction, and polarisation.

The second point is of considerable importance. At the present time, some hundreds of opticians present themselves annually for the examinations of the Spectacle Makers' Company and the British Optical Association, and it is extremely difficult for these candidates to obtain satisfactory instruction, owing to the small number of teachers who have given attention to spectacle optics. It would greatly increase the efficiency of these opticians if the teaching of optics in all the science centres were suited to their needs, and it would also be advantageous if all those who studied optics were familiar with the language and methods employed by the opticians. Unless, therefore, there is good reason for separating scientific teaching from the trade methods, it is highly desirable that the teaching in all the centres should be suitable for opticians. Indeed, as the methods of opticians are in complete harmony with physical optics, it is difficult to justify the separation.

In view of the long time which has elapsed since this question was last discussed, it appears desirable to recapitulate briefly the main features of the wave treatment; referring those specially interested to the papers above cited.

## § 2. ELEMENTARY OPTICS

*Nature and propagation of light.* The propagation of transverse waves is shown by a ripple tank, which may advantageously be illuminated stroboscopically so that the apparent rate of propagation may be slowed down. The Huygens explanation of approximately rectilinear propagation can be well shown by employing multiple sources and increasing their number until they become a practically linear source. Elementary ideas on interference diffraction and polarisation may usefully be introduced at the outset; and the pinhole camera serves as an introduction to magnification in optical systems.

*Illumination and photometry.* Each wave contains a certain amount of light energy, and the energy per unit area of wave surface or illumination therefore diminishes as the square of its radius. Oblique illumination and the cosine law follow from the projected area of the surface.

*Reflection at plane surfaces.* Huygens's construction for plane waves. Position and size of image follows from symmetry of wave fronts before and after reflection.

*Curvature theory and notation.* Curvature  $R$  is defined as the angle turned through per unit length of arc, and proved to be the reciprocal of the radius  $r$ , or  $R = 1/r$ . The unit of curvature is the dioptré or curve of 1 metre radius, so that

$$R_{\text{dioptrés}} = 1/r_{\text{metres}} = 100/r_{\text{cm}} = 39.37/r_{\text{inches}}.$$

It is desirable to exhibit a curve of 1 metre radius, so that this curvature may

be visualised and to point out that for a chord of 9 cm. (more accurately 8.95 cm.) the curvature in dioptries is represented by the sag in millimetres.

*Measurement of curvature, spherometer.* In any circle by Euclid III, 35,

$$(2r - s)s = c^2,$$

where  $s$  is the sagitta or "sag" at the centre of a chord of length  $2c$ . Hence

$$R = 1/r = 2s/(c^2 + s^2).$$

If  $s < c/10$ ,  $R = (2/c^2)s$  within 1 per cent.,

so that for a given length of chord the curvature is proportional to the sag. If  $R$  is to be in dioptries  $s$  and  $c$  must be in metres, but if they are expressed in centimetres  $R = (200/c^2)s$ . It should be emphasised at this point that the approximation is only justified for short chords or small apertures, and that as the chord or aperture is increased the term  $h^2$  becomes more important, the way being thus paved for the later study of aberrations. The ordinary and direct reading dioptric spherometers are then explained.

The curvature theory and notation apply equally to reflecting or refracting surfaces and to wave fronts, and the most convenient convention for the latter is to consider all convergent waves as of positive curvature, and to speak of that curvature as the convergence in dioptries, irrespective of the direction of travel.

*Reflection at curved surfaces.* If a plane wave impinges on a concave mirror the sag of the wave front after reflection is evidently double that of the mirror, so that the convergence  $F = 2R$  where  $R$  is the curvature of the mirror. If the incident wave has convergence  $U$  or  $1/u$ , the distance between the wave front and mirror for a given chord is proportional after reflection to  $U + R$ , which  $= V - R$ . Hence

$$V - U = 2R = F,$$

corresponding to the ordinary relation for conjugate foci

$$1/v - 1/u = 2/r = 1/f,$$

except for the change of sign of  $V$ . A concave mirror always has positive, and a convex mirror negative convergence. Magnification may be treated in the ordinary manner, but the most simple general method is to consider the mirror stopped down to a pinhole at the vertex, in which case

$$m = v/u = U/V,$$

from the pinhole camera relation. The effects of reflection at concave surfaces may be particularly well illustrated with the ripple tank, stroboscopic illumination being used, as if the frequency of the flashes is a little less than that of the waves there is an apparent slow progress from the source to the conjugate focus, while if the frequency is increased the waves appear to travel in the opposite direction, clearly showing the conjugate principle.

*Refraction at plane surfaces.* The velocity of light being assumed to be reduced in dense media, Huygens's proof of the sine law

$$\sin \theta / \sin \phi = V_1/V_2 = \mu_2/\mu_1 = \mu$$

is given, and may be illustrated by the ripple tank, and by the idea of ranks of men

marching obliquely towards and crossing a river. If these ranks are made up of tall men in red uniforms and short men in blue, the reason for dispersion is clearly seen. Thick prisms are treated in the ordinary manner, but the relations

$$\theta_1 + \theta_2 = \delta + \alpha, \text{ and } \phi_1 + \phi_2 = \alpha$$

are more easily seen when wave fronts are used instead of rays. Thin prisms are particularly simple: since while the wave traverses a thickness  $t$  of glass it would traverse a distance  $\mu t$  in air, it is retarded by the distance  $(\mu - 1)t$  so that

$$\delta = (\mu - 1) \alpha,$$

where  $\delta$  is the deviation and  $\alpha$  the angle of the prism. The optician generally expresses the deviation of thin prisms in "prism dioptres" or the number of centimetres displacement in a metre, so that one prism dioptre,  $1\Delta$ , is 0.01 radian or 0.573 degree.

When spherical waves pass from one medium to another we evidently have the relation

$$\mu_1 s_1 = \mu_2 s_2 \text{ or } \mu_1 U = \mu_2 V,$$

so that

$$V = (\mu_1/\mu_2) U = U/\mu.$$

This gives the "apparent thickness" of a block of glass, and the "microscope method" of measuring refractive indices. The quantity  $\mu s$  may be called the "optical sag," and all problems of refraction may be dealt with by the principle that when waves pass from one medium to another the optical sags of the incident and refracted wave fronts are equal.

*Refraction by thin spherical lenses.* Since the retardation of a wave in passing through a thickness  $t$  of medium of refractive index  $\mu$  is  $(\mu - 1)t$ , it follows immediately that in passing through a lens the change of convergence

$$V - U = (\mu - 1) C = (\mu - 1) (R_1 + R_2) = F,$$

where  $R_1$  and  $R_2$  are the curvatures of the two faces and  $C$  or  $(R_1 + R_2)$  is the "total curvature" of the lens. This is equivalent to the ordinary formula

$$1/u - 1/v = (\mu - 1) (1/r_1 - 1/r_2) = 1/f,$$

but with reversal of sign of  $1/r_2$ , the reason being that in the case of a double convex lens both surfaces converge the light and are therefore reckoned as positive. The relation

$$F = (\mu - 1) (R_1 + R_2)$$

may be written

$$F = (\mu - 1) R_1 + (\mu - 1) R_2 = F_1 + F_2,$$

where  $F_1$  and  $F_2$  are the "surface powers" of the lens, which may be measured directly by a "Geneva lens measurer." This instrument is a direct reading spherometer having two fixed points and a third sliding point midway between them, which point is geared to a pointer moving round a scale and is pushed outwards by a spring. When the three points are pressed against a plane surface the pointer registers zero on the scale, but if the surface is convex or concave it indicates the "surface power" (positive or negative) on the assumption that the index of refraction

tion of the glass is about 1.52—the ordinary value for spectacle glass. Two fixed points are used instead of the three of the ordinary spherometer, in order that it may be possible to measure cylindrical or toric lenses. In measuring thin spherical lenses the instrument is applied to both faces, and the power of the lens is the algebraical sum of the readings.

The optician is concerned with the form of lenses as well as their power, as meniscus lenses are generally preferable for spectacles. The above treatment shows at once that the form of a lens of any given power may be varied to any extent by pushing in one face and pulling out the other, so long as the central thickness or total curvature remains the same. The optician is also concerned with cylindrical, sphero-cylindrical, and toric lenses and their transposition, and these subjects can be most simply dealt with on the above lines. The magnification of the image is obtained as with mirrors by supposing the lens to be stopped down to a pinhole, giving the same relation

$$m = v/u = U/V.$$

*Decentration.* Another important matter is the combination of lenses with prisms to correct defects of convergence in the eyes. A convex lens of convergence  $F$  or  $100/f_{\text{cm}}$  dioptres brings all axial parallel light to a focus on its axis at a distance of  $f_{\text{cm}}$ , so that a ray at a distance  $d_{\text{cm}}$  from the axis is deviated  $d_{\text{cm}}$  in  $f_{\text{cm}}$  or  $100d/f$  or  $Fd_{\text{cm}}$  in a metre, which is the prismatic effect  $\Delta$  in prism dioptres. Hence

$$\Delta = Fd, \text{ or } d = \Delta/F,$$

so that the decentration in centimetres required to produce a given prismatic effect is obtained by dividing the number of prism dioptres required by the power of the lens in dioptres. The base of the prism is in the same direction as the decentration with convergent lenses, but in the opposite direction with divergent lenses.

*Thin lenses in contact. Neutralisation.* In the dioptric notation, the power of any number of thin lenses in contact is obviously the algebraic sum of their individual powers; provided, of course, that the total thickness of the combination is small. This fact, in combination with the prismatic effect of decentration, is the basis of the opticians' method of measuring the powers of lenses by "neutralisation." The lens to be tested is held before the eye and some distant object and is moved vertically or horizontally. The object will appear to move in the same direction as the motion of the lens if the lens is convergent, but in the opposite direction if it is divergent. Known lenses of opposite power are then taken from a trial case and combined with the lens to be tested until the apparent motion is neutralised.

*Effect of axial displacement.* The convergence of a spherical wave obviously increases as it travels towards its focus. If its initial convergence is  $F$  dioptres and it travels forward a distance  $d$  metres, its convergence will be

$$F' = 1/(f - d) = F/(1 - Fd)$$

dioptres. This is of some importance in spectacle optics, owing to the varying displacement of lenses from the eye; and it forms an introduction to the theory of separated lenses, thick lenses, and lens combinations.

## § 3. LENS COMBINATIONS

*Separated thin lenses.* If we have two lenses of powers  $F_1$  and  $F_2$  dioptries separated by a distance  $d$  metres, and parallel light falls axially on the first, the convergence of the light reaching the second lens will be  $U_2$  or  $F_1/(1 - F_1 d)$  dioptries, and

$$V_2 = F_1/(1 - F_1 d) + F_2 = (F_1 + F_2 - F_1 F_2 d)/(1 - F_1 d)$$

dioptries after passing through it. This corresponds to the ordinary formula for the "back focus,"  $(f_1 + f_2 - d)/(f_2(f_1 - d))$ . If we have a distant object subtending an angle  $\alpha$ , the first lens would form an image of length  $f_1 \alpha$  or  $\alpha/F_1$ , and this will be magnified by the amount  $m_2$  where

$$m_2 = U_2/V_2 = F_1/(F_1 + F_2 - F_1 F_2 d)$$

by the second lens, giving the size of the final image as

$$\alpha/(F_1 + F_2 - F_1 F_2 d).$$

But if we have a single lens of power  $F$  dioptries the size of the image will be  $\alpha/F$ , and if this is to be equal to that given by the combination,

$$F = (F_1 + F_2 - F_1 F_2 d),$$

which is therefore the equivalent power of the combination, corresponding to the formula  $f = f_1 f_2 / (f_1 + f_2 - d)$  for the equivalent focal length.

*Refraction at a single spherical surface.* In dealing with thin lenses we considered the effect of the lens as a whole, without troubling about the separate surfaces, but for thick lenses and combinations the refraction at each surface must be considered separately. If we have a convex surface of curvature  $R_0$  between two media of refractive indices  $\mu_{-1}$  and  $\mu_{+1}$  then, by the principle of equality of the optical sags,

$$\mu_1 (V_1 - R_0) = \mu_{-1} (U_{-1} - R_0), \text{ or } \mu_1 V_1 - \mu_{-1} U_{-1} = (\mu_1 - \mu_{-1}) R_0 = F_0.$$

Also if we consider a pinhole aperture at the vertex,

$$m = v \tan \phi / u \tan \theta = v \sin \phi / u \sin \theta = \mu_{-1} v_1 / \mu_1 u_{-1} = \mu_{-1} U_{-1} / \mu_1 V_1.$$

Using von Seidel's notation we may denote  $\mu_{-1} U_{-1}$  by  $U'_{-1}$ , the "reduced" convergence, and  $\mu_1 V_1$  by  $V'_1$ , from which we have

$$V'_1 - U'_{-1} = (\mu_1 - \mu_{-1}) R_0 = F_0, \text{ and } m = U'_{-1} / V'_1.$$

*Thick lenses and lens combinations.* If we have a thick lens of curvatures  $R_0$  and  $R_2$  and thickness  $d_1$ , then at the first surface

$$V'_1 - U'_{-1} = F_0 \text{ and } m_0 = U'_{-1} / V'_1$$

as above. In traversing the lens the convergence  $V_1$  will increase to

$$U_1 = V_1 / (1 - V_1 d_1),$$

from which

$$U'_1 = \mu_1 U_1 = \mu_1 V_1 / (1 - V_1 d_1) = \mu_1 V_1 / \{1 - \mu_1 V_1 (d_1 / \mu_1)\} = V'_1 / (1 - V'_1 d'_1),$$

if  $d'_1 = d_1 / \mu_1$ . But  $d_1 / \mu_1$  is the "apparent" thickness of the lens so that if we employ



"reduced" convergences and "apparent" thicknesses, the formulae for thick lenses are identical with those for separated combinations of thin lenses.

From the three formulae

$$V_+' - U_+' = (\mu_+ - \mu_-) R = F, \quad m = V_+/U_-, \quad \text{and} \quad U_+' = (V_+'/(1 - V_+'d')),$$

we can obtain the Gauss formulae for lens combinations and the positions of the principal, focal, and symmetrical planes, and nodal points, as described in the Physical Society paper above cited.

#### § 4. ABERRATIONS

Only a short sketch of the leading points of aberration theory can be given here, but a fairly complete theory has been given in the Traill Taylor lecture above cited.

*Chromatic aberration.* Since for a thin lens  $F = (\mu - 1) C$ ,

$$\Delta F = C \Delta \mu = F \cdot \Delta \mu / (\mu - 1) = F/\nu,$$

where  $\nu$  is the "efficiency" of the glass and

$$\nu = (\mu - 1)/\Delta \mu.$$

If we have two thin lenses in contact

$$F = F_1 + F_2, \quad \text{or} \quad \Delta F = \Delta F_1 + \Delta F_2 = F_1/\nu_1 + F_2/\nu_2.$$

Hence for an achromatic combination

$$F_1 + F_2 = F, \quad \text{and} \quad F_1/\nu_1 + F_2/\nu_2 = 0,$$

from which

$$F_1 = \frac{\nu_1}{\nu_1 - \nu_2} F, \quad \text{and} \quad F_2 = -\frac{\nu_2}{\nu_1 - \nu_2} F.$$

*Spherical aberration.* In dealing with the theory of curvature, it was pointed out that the sag was only proportional to the square of the chord for small apertures. To determine it for large apertures suppose a convergent wave  $U$  falls on a surface of curvature  $R$ . Then in the annexed diagram, Fig. 1, the sag

$$s = u - u', \quad \text{and} \quad u'^2 = r^2 + (u - r)^2 + 2r(u - r) \cos \alpha.$$

If  $h$  is the oblique distance from the point considered to the vertex

$$\sin \alpha/2 = h/2r, \quad \text{and} \quad \cos \alpha = 1 - h^2/2r^2,$$

from which

$$u'^2 = u^2 - h^2(u - r)/r$$

$$\text{and} \quad s = u - \sqrt{u^2 - h^2(u - r)/r} = u \{1 - \sqrt{1 - U(R - U)/h^2}\}.$$

Expanding, we have

$$s = (R - U) h^2/2 + U(R - U)^2 h^4/8 + U^2(R - U)^3 h^6/16 + \text{etc.}$$

Hence the "optical sag"

$$s_1' = \mu_1 s_1 = \mu_1 (R - U) h^2/2 + \mu_1 U(R - U)^2 h^4/8 + \mu_1 U^2(R - U)^3 h^6/16 + \text{etc.}$$

If we now assume for the moment that the wave front after refraction is spherical and of curvature  $V$ , then by the same reasoning

$$s_2' = \mu_2 s_2 = \mu_2 (R - V) h^2/2 + \mu_2 V (R - V)^2 h^4/8 + \mu_2 V^2 (R - V)^3 h^6/16 + \text{etc.}$$

For this to be true  $s_2' = s_1'$  or  $s_2' - s_1' = 0$ , but from the above

$$\Delta s' = s_2' - s_1' = \{\mu_2(R-V)^2 - \mu_1(R-U)\} \hbar^2/2 \\ + \{\mu_2 V(R-V)^2 - \mu_1 U(R-U)^2\} \hbar^4/8 \\ + \{\mu_2 V^2(R-V)^3 - \mu_1 U^2(R-U)^3\} \hbar^6/16 + \text{etc.}$$

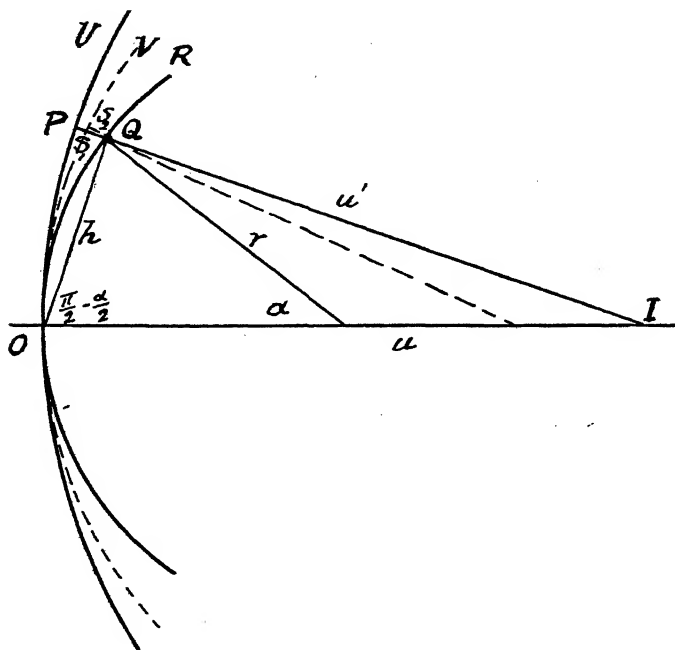


Fig. 1.

The first term vanishes when

$$\mu_2 V - \mu_1 U = V' - U' = (\mu_2 - \mu_1) R = F_1,$$

the ordinary relation for small apertures, but this does not make the higher terms vanish, and we therefore have:

### First order spherical aberration

$$\Delta s' = \{\mu_2 V (R - V)^2 - \mu_1 U (R - U)^2\} \hbar^4/8.$$

### Second order spherical aberration

$$\Delta s' = \{\mu_2 V^2 (R - V)^3 - \mu_1 U^2 (R - U)^3\} h^6/16, \text{ etc.}$$

Where  $\Delta s'$  in each case is the departure of the wave front from the spherical form, measured normally to the sphere in optical distance or wave lengths. It should be noticed that this exactly corresponds with the measurement of aberrations by the Hilger lens testing interferometer, and that it enables the interferograms

obtained with this instrument to be directly interpreted. Objection has been taken to this method, owing to the complicated form which the distorted wave front takes as it advances towards the "focus"; but if the aberration is small this is not of importance, while if it is large, it must be corrected before it has advanced very far, so that the objection has no practical weight. In dealing with the spherical aberration of a lens system, it is only necessary to trace the course of a pencil approximately through the system, and to calculate  $\Delta s'$  at each surface; the total displacement of the wave front from the spherical form after emergence being the algebraic sum of the displacements at the several surfaces.

*Oblique aberrations.* Before dealing with these generally, it is useful to familiarise students with the general character of such aberrations by taking the simple case of a single thin convergent lens. It was shown above that the power of such a lens

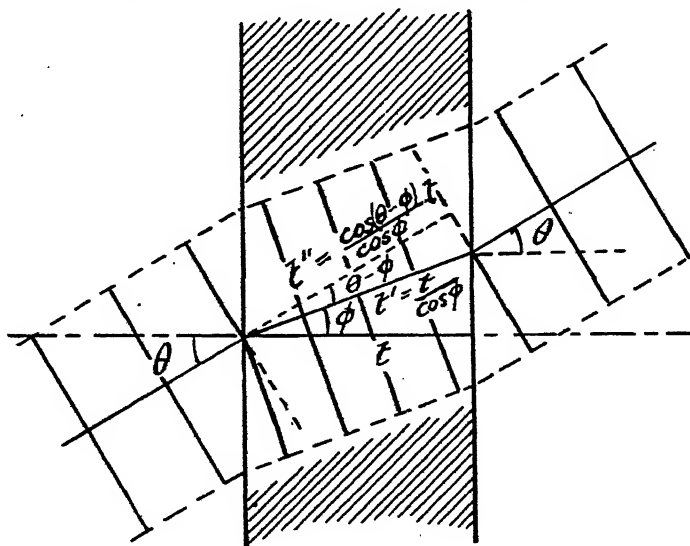


Fig. 2.

could be directly obtained by considering the retardation of the centre of the wave front on passing through the glass. If we have a parallel plate of glass of thickness  $t$  as in Fig. 2 and consider plane waves falling on one surface inclined at an angle  $\theta$ , the actual distance traversed through the glass is  $t/\cos \phi$  where  $\phi$  is the inclination of the refracted wave to the surface, and in the time taken to traverse this distance the wave would have advanced by  $\mu t/\cos \phi$  in air. The actual distance travelled by the wave front will however be  $(t/\cos \phi) \cos(\theta - \phi)$  owing to the change of inclination, and the retardation is therefore

$$\mu t/\cos \phi - t \cos(\theta - \phi)/\cos \phi = (\mu \cos \phi - \cos \theta) t,$$

as compared with  $(\mu - 1) t$  for axial light. The ratio of the oblique to the axial retardation is therefore

$$(\mu \cos \phi - \cos \theta)/(\mu - 1) = 1 + \theta^2/2\mu,$$

when  $\theta$  is small. Applying this to the thin lens, we find that the power in the sagittal

plane is increased in the ratio  $1 + \theta^2/2\mu$ . But in the meridional plane the obliquity of the wave front causes the same retardation to be given to a beam which is narrower in the ratio  $\cos \theta$ , so that the curvature is increased in the ratio  $1/\cos^2 \theta = 1 + \theta^2$ , when  $\theta$  is small. Hence we have:

$$\text{Power in meridional plane} = F(1 + \theta^2/2\mu)(1 + \theta^2) = F\{1 + \theta^2(2\mu + 1)/2\mu\}.$$

$$\text{Power in sagittal plane} = F(1 + \theta^2/2\mu).$$

The lens therefore acts as a sphero-cylindrical lens of spherical power  $F(1 + \theta^2/2\mu)$  and cylindrical power  $F\theta^2$ , the axis of the cylinder being parallel to the axis about which it is tilted—a result which is useful to the spectacle optician. It is easy from this to work out the curvature of the primary and secondary focal surfaces, and to give clear ideas of astigmatism and curvature of the field; and as the wave front meets the lens asymmetrically, some idea of coma can be formed. This simple

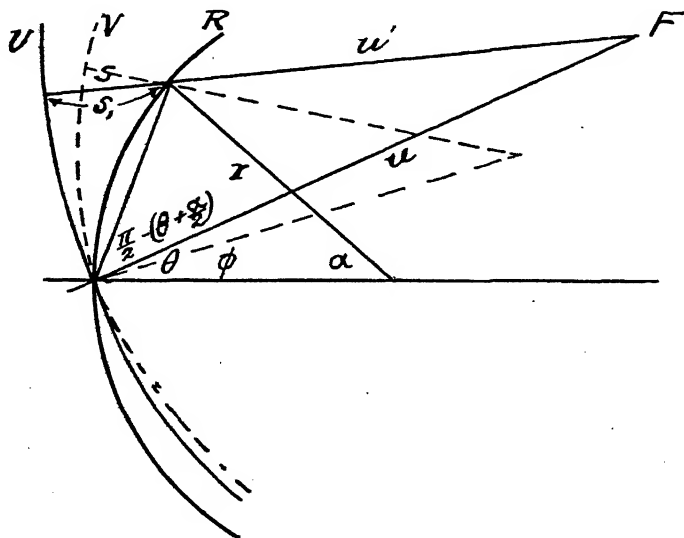


Fig. 3.

treatment strikingly exhibits the advantages of the wave method, as no other method enables the idea and magnitude of the oblique aberrations to be so easily demonstrated.

*Oblique refraction at a spherical surface.* After the above introduction and the treatment of axial spherical aberration, the calculation for oblique refraction at a single surface is a relatively easy matter. In the annexed diagram, Fig. 3, we have the same conditions as in Fig. 1 except that the axis of the incident wave front  $U$  is inclined at an angle  $\theta$  to the radius of the refracting surface at the point of incidence. We then have:

$$u'^2 = u^2 + h^2 - 2uh \cos \{\pi/2 - (\theta + \alpha/2)\} = u^2 - \{2u \sin (\theta + \alpha/2) - h\} h,$$

and expanding as before, and putting

$$\sin \alpha/2 = Rh/2, \text{ and } \cos \alpha/2 = 1 - R^2h^2/8 - R^4h^4/128, \text{ etc.}$$

we have

$$s_1 = \sin \theta \cdot h + (R \cos \theta - U \cos^2 \theta) h^2/2 + \{U(R \cos \theta - U \cos^2 \theta) - R^2/4\} \sin \theta h^3/2 \\ + \{U[R \cos \theta - U \cos^2 \theta \{R \cos \theta - U(1 - 5 \sin^2 \theta)\} - R^2 \sin^2 \theta]\} h^4/8 + \text{etc.}$$

which reduces to the same expression as that obtained for the axial pencil when  $\theta = 0$ .

If, as before, we assume that the refracted wave front is circular and of curvature  $V$  we have

$$\Delta s' = s_2' - s_1' = \mu_2 s_2 - \mu_1 s_1 = (\mu_2 \sin \phi - \mu_1 \sin \theta) h \\ + \{\mu_2 (R \cos \phi - V \cos^2 \phi) - \mu_1 (R \cos \theta - U \cos^2 \theta)\} h^2/2 \\ + [\mu_2 \{V(R \cos \phi - V \cos^2 \phi) - R^2/4\} \sin \phi \\ - \mu_1 \{U(R \cos \theta - V \cos^2 \theta) - R^2/4\} \sin \theta] h^3/2 + \text{etc.}$$

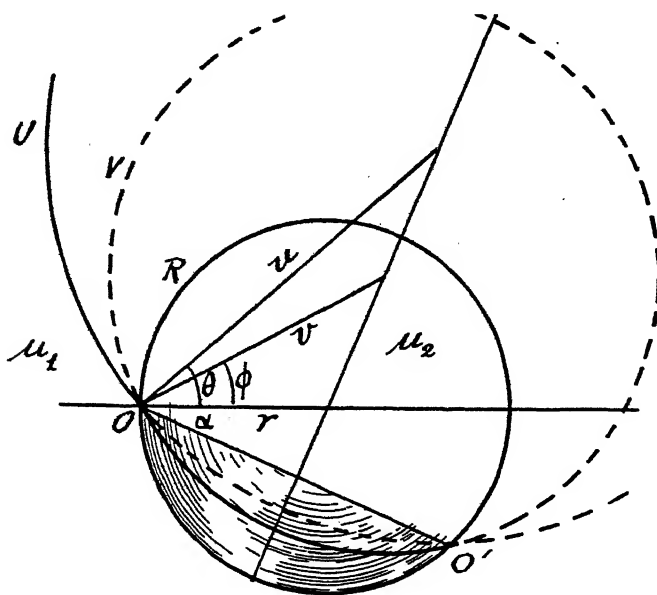


Fig. 4.

The first term vanishes when  $\mu_2 \sin \phi = \mu_1 \sin \theta$ , the ordinary law of refraction, and the second vanishes when

$$\mu_2 V \cos^2 \phi - \mu_1 U \cos^2 \theta = V' \cos^2 \phi - U' \cos^2 \theta = (\mu_2 \cos \phi - \mu_1 \cos \theta) R;$$

leaving the third term, which is obviously asymmetrical, to give the optical displacement of the wave front due to coma.

The above calculation applies only to the meridional plane. For the sagittal plane a similar process may be adopted, but for the first approximation a more simple method may be employed. In Fig. 4 the whole of the spherical surface  $R$  is shown, with the two wave fronts  $U$  and  $V$  intersecting it at the points  $O$  and  $O'$ .

If we consider the sphere cut through by a plane  $OO'$ , the circular section will have a radius  $r \cos \alpha$ , and considering the wave fronts as spheres we have evidently

$$u \cos (\theta + \alpha) = v \cos (\phi + \alpha) = r \cos \alpha,$$

from which

$$\cos \theta - \sin \theta \tan \alpha = r/u = U/R \quad \text{and} \quad \cos \phi - \sin \phi \tan \alpha = V/R,$$

and since

$$\mu_1 \sin \theta = \mu_2 \sin \phi,$$

$$\mu_2 V - \mu_1 U = V' - U' = (\mu_2 \cos \phi - \mu_1 \cos \theta) R$$

for the sagittal plane, as compared with

$$\mu_2 V \cos^2 \phi - \mu_1 U \cos^2 \theta = V' \cos^2 \phi - U' \cos^2 \theta = (\mu_2 \cos \phi - \mu_1 \cos \theta) R$$

for the meridional plane. It is easy to show that these results agree with those obtained from the simple treatment of the thin lens.

The expression for coma becomes

$$\Delta s' = \{V(R \cos \phi - V \cos^2 \phi) - U(R \cos \theta - U \cos^2 \theta)\} \mu_1 \sin \theta h^3/2.$$

Distortion may be considered to the first approximation as spherical aberration of the exit pupil, and therefore requires no fresh treatment.

In the author's own lectures, a method of tracing and summing the aberrations through a system was developed, analogous to the method of von Seidel; but this has not been published, and it would involve too much space to be given here. Enough has, however, been said above to show that the wave or curvature method can be employed with advantage for the treatment at least of first order aberrations, and the harmony of this method with the indications of the lens testing interferometer is a feature which must commend it. For the final design of large aperture systems, ray tracing is undoubtedly necessary, but this presents no difficulty to students who have followed the wave method to this stage, and hardly justifies the idea that geometrical methods should be adopted at an early stage to provide for this particular application. The diffraction phenomena at and near the focus can of course be readily comprehended from the form of the wave front.

It is unnecessary to carry the treatment further into the field of physical optics in the present paper as the whole method has been physical from the outset and there is therefore no discontinuity to be bridged. Brief and imperfect as this sketch has necessarily been, it is hoped that it will convince many teachers of the practicability and advantages of systematic optical teaching by the wave method, and that an increasing number will adopt it, with the result of making their teaching suitable for science students and opticians alike.

## 7. FIRST STEPS; THE PROBLEM OF THE BEGINNER

By V. T. SAUNDERS, M.A.

*ABSTRACT.* The general conditions which a school course in geometrical optics must satisfy are considered, and a method of presentation which has been suitable for teaching beginners is outlined. It is pointed out that there is no time available during school life for a serious course in geometrical optics beyond the investigation of the ideal lens, and also that even if there were time the boys have not sufficient mathematical equipment to handle the problems involved. The suggestion is made that more attention might be paid in the initial stages to the simpler conceptions of physical optics, more especially for those boys who will not specialise in science.

SCIENCE masters in schools must approach this problem as learners. We have to survey the whole accumulated body of knowledge of light and decide how boys may be introduced to it; after a selection of material suitable to form an introduction we have to consider how it may best be presented in order that a true appreciation of the principles of the subject may be grasped.

In making our selection of material and formulating our method of presentation we have to be guided by our knowledge that it is only a small percentage of our boys who will become professional scientists, and that the vast majority will follow other callings in life; they will be the people who will avail themselves of the facilities which science provides to assist them in their lives, but they will not make any contribution to the advancement of knowledge in the abstract, nor to the improvement of technical methods. Again we have to bear in mind that youth is more concerned to do than to think but that the faculty of thinking can be stimulated by interest in doing. It follows from these considerations that a school science course must satisfy two conditions: (i) it must be complete in itself as far as it goes, dealing with general principles and widespread applications; (ii) it must be a sound foundation on which those who carry on subsequent study, may build. In this present discussion we are concerned to discover if this second condition is, in fact, satisfied by the courses at present followed in schools.

A school course must begin with the concrete and work towards the abstract. The sunbeam offers us a concrete starting point; it becomes a ray and its path can be followed. Straight line propagation and parallax are accepted and the study of lenses can be started. We give a boy a lens and lead him to discover what it will do. I find by experience that this method can be followed without any discussion of the sine law of refraction. The image-forming property is arresting, and its various aspects are soon discovered and appreciated. Combinations of two lenses follow easily, and a simple telescope and microscope are soon made and understood. We work from the parallel ray definition of the principal focus, and from the magnification property; the formulae involving reciprocals are avoided, and all

quantitative work is done by drawing ray diagrams by the collinear method. Plane and curved mirrors are investigated in the same way. When boys handle lenses, microscopes and telescopes, they learn the language of the subject, and also the potentialities and limitations of the instruments; familiarity with things that are leads them to ponder over what might be. This initial stage must be largely experimental; the demonstration experiments can be well shown with a piece of apparatus known as the "optical disc" (which is supplied by a number of apparatus firms) and by the smoke box. The laboratory experiments for the boys can be carried out with apparatus which costs very little.

This method of treatment may be retained up to the First School Examination, but it appears that the method of procedure to be followed by those boys who stay at school up to the age of 18-19 years and go to a university to read science, is the main question under discussion. At present the general method followed in schools, in teaching geometrical optics, is to accept the spherical surface of refraction and to ignore the defects of the images formed by it. This undoubtedly leads to failure to appreciate the actual powers and limitations of optical instruments. On the other hand we in schools must teach general principles and the extent to which we can follow out the technique of geometrical optics is strictly limited. It can be argued with much justification that the educational value of physical optics might be explored more fully, and that, for a general education, knowledge of the simpler aspects of physical optics gives a broader outlook on the field and method of science than is provided by an intensive study of the technical knowledge involved in the design of optical instruments.

However, after the First School Examination stage a number of important points have to be faced: (i) the sign convention; (ii) the introduction of the wave conception; (iii) the differences between the ideal lens and the actual lens. With regard to the first, I find that after boys have been started on ray diagrams they find little or no difficulty with the sign convention which accepts as positive, distances measured against the direction of the incident light; boys using the reciprocal formulae almost invariably draw a freehand diagram to aid them in fixing their signs. I have considered the other, and sometimes simpler, conventions for the initial stages, but I am unable to see that any advantage is gained in not accepting the convention which is at present found in all advanced text-books. If, in the future, the methods and conventions of the university text-books change, it will, I think, be necessary to modify our methods (in this second stage) in order that uniformity may be reached.

On the question of the introduction of the wave conception, I find that it comes most easily after a discussion of the velocity of light. The development of the reciprocal formulae from wave-fronts, for small apertures, involves no difficulties at this stage. The properties of waves and the effect of change of the velocity of propagation of waves can be adequately demonstrated by a ripple trough illuminated by a point-o-lite lamp. The simpler experiments showing interference fringes can be demonstrated with advantage, and an estimation of the wave-length of light arrived at.



On the question of the actual, as opposed to the ideal lens, very little is taught in schools: the mathematical equipment necessary for the solution of the problems involved is usually not to be found in schoolboys. But if a simple method of presenting this branch of the subject is disclosed it will certainly find its way into school work.

I have tried to point out what is being done in schools at present, and to give reasons for our methods. No attempt is made to justify the present procedure; it remains for those who consider that our methods are not the best, to indicate how we may improve; the school science master must keep an open mind on these matters, and modify his methods to conform with the progress of knowledge.

Finally I would plead for the retention of optics as a school subject. It is sometimes said that because we cannot teach boys the more exact methods and processes of the technical aspect of the subject, it is better not to teach it at all. I believe that this attitude is based on a misconception of the function of school education, and that it is detrimental to the progress of science. The school education gives a boy an insight into the things that are being done in the world, it enables him to be in sympathy with the work carried out by researchers, and it supplies the best means by which the general body of public opinion may learn to accept scientific research and its applications to industry, as essential factors for the continuance and for the development of the present civilisation.

## 8. AN ELEMENTARY COURSE ON LIGHT BASED ON THE WAVE THEORY

C. G. VERNON, Bedales

**ABSTRACT.** The writer describes his experience in teaching light from the beginning from the point of view of the wave theory, a method which he states to be both possible and easy. Starting from a consideration of waves, illustrated by means of wave-machines and a ripple-tank, he develops Huyghens' principle and investigates thoroughly the phenomena of propagation in straight lines, plane reflection and refraction, and the simple theory of the function of glass blocks, lenses and spherical mirrors. Besides giving a good grounding in these fundamentals, the method leads naturally to the study of the spectrum and the more advanced phenomena. The writer indicates the development of the mathematical side with the use of curvatures, and suggests that the correct rôle of geometrical optics is to serve for the revision and coordination of work already done. He indicates difficulties that arise over sign conventions, and states that this is a distinct drawback to the teaching. Finally he makes a plea for the carrying out of practical work by beginners with real beams of light, as distinct from the misleading and uninteresting methods known as "pin and parallax."

BEING dissatisfied with the accepted methods of teaching elementary light I devised a method of approaching the subject from the point of view of the wave theory. This was taught to pupils who had completed two years of physics in a secondary school course, and proved to be highly successful. The following account tells of my objections to the older methods together with the advantages I consider this method to possess, an outline of the elementary part of the course and of the mathematical development of it, the very real difficulties that exist over sign conventions, some criticisms of the course and a reference to methods of demonstration and practical work.

In drawing up the course I derived considerable help from the late Silvanus Thompson's book, *Light, Visible and Invisible*. I have embodied my experience in a text-book that has recently been published by the Cambridge University Press, and which contains an amplification of the points set out below.

### § 1. OBJECTIONS TO ORTHODOX METHODS

1. Lack of interest. The lessons tend to become sterile and lifeless.
2. The theory is almost entirely mathematical, and has little or no reference to the physical nature of light.
3. The reasoning involved is restricted in nature, and there is no scope for the exercise of controlled imagination, which is, or should be, one of the essentials of the teaching of physics in schools.

## § 2. ADVANTAGES OF THE NEWER METHOD

1. Interest.
2. The physical nature of light is made the basis of a very thorough grounding in the essentials of: propagation; plane reflection; plane refraction (and total reflection); function of lenses and mirrors; colour; relation to radiant heat.
3. The reasoning is varied, and so makes a wider appeal than does that of the other method.
4. Light ceases to be in a water-tight compartment, but takes its place as a branch of physics, related to heat, properties of matter, electricity and modern views on the constitution of matter.
5. The necessary introduction to the study of waves is a valuable thing in itself, and also serves as an introduction to sound.

## § 3. OUTLINE OF THE COURSE

(a) Nature of wave-motion; simple harmonic motion. Distinction between motion of wave and movement of particles of the medium. Transverse and compression waves.

Wave length; frequency; velocity of wave; amplitude.

(b) Ripples on water (ripple tank). Disturbance from one point and simultaneously from many points in a line, giving circular and straight-line wave-fronts.

Effect of isolating a small portion of the wave-front. Huyghens' principle and constructions based on it.

(c) Use of Huyghens' principle to investigate the persistence of shape of a wave in a uniform medium. Concave wave-fronts and the existence of a focus.

(d) Plane reflection of straight-line and circular waves (1) from the construction, (2) as seen in the tank. Effect of introducing a sheet of glass into the tank and so producing a second (shallower) medium differing from the first. Refraction of straight-line and circular waves due to a difference in velocity.

(e) Applications to light. Straight-line and circular ripples correspond to plane and spherical waves in space. Effect of the increasing area of a spherical wave—inverse square law and simple photometer. Parallel, diverging and converging beams of light.

Plane reflection and position of the image.

(f) The "refraction roller" experiment to illustrate refraction of a plane wave. The velocity constant, a physical constant of the medium.

Huyghens' construction used for refraction of a plane wave. Apparent depth of water due to refraction of a spherical wave. Concept of a ray as "a line representing the direction of movement of an element of the wave-front." Use of rays for simplification of diagrams.

*N.B.* Avoid referring to "a ray of light."

(g) Shadows. (Mention difficulty about shadows and waves.) Umbra, penumbra, eclipses, etc.

(h) Simple refraction problems. Parallel-sided glass block. Semicircular glass block, critical angle and total reflection. In each case investigate (1) with roller, (2) by Huyghens' construction, (3) with light, e.g. smoke box.

Mention Snell's law at this point, using  $\mu$  as a mathematical ratio.

Other cases may then be dealt with, namely ghost images in a thick mirror, total reflection prism, fish-eye view, mirage, setting sun, etc.

(i) Effect of reflecting straight-line waves at a circular surface—imprinting of curvature.

Illustrate in a tank, by Huyghens' construction, and by means of beams of light on spherical mirrors in a smoke box.

(j) Functions of lenses, imprinting of curvature due to slowing down of either centre or periphery of a portion of wave-front. Types of lens. Illustrate by smoke box and draw both wave and ray diagrams.

As may be judged, the student may by now be assumed to be familiar with the fundamental phenomena of propagation, reflection and refraction and their consequences, and the mode of operation of lenses and spherical mirrors. The criticism may be levelled that it is not possible for the students to do much practical work that has any close bearing on the theory of matter, but the drawing of the wave diagrams is certainly just as much "practical light" as is the "fixing of rays by means of pins" (1); and, using narrow beams of light (such as may be obtained by means of the "Rugby" optical apparatus) the beginner may do the qualitative demonstrations of the behaviour of light that have been indicated above.

#### § 4. MATHEMATICAL DEVELOPMENT

There are now two courses open. By the use of the wave concept it is possible to establish all the important relations by means of simple proofs that are easily followed by children of reasonable intelligence. A summary of the more important points of the method may be of interest.

Call the velocity-constant (i.e. velocity in air  $\div$  velocity in medium),  $h$ .

Use the definition, curvature = reciprocal of radius, and then establish the relation, sagitta = curvature  $\times$  a constant.

Focal power, denoted by  $F$ , is taken as the curvature imparted to any wave by the given lens or mirror, and is measured by the curvature given to a plane wave (whence  $F = 1/f$ ).

The following may be shown:

1. Position of image behind a plane mirror.

Sagittae of incident and reflected waves are equal but of opposite sign, whence

$$v = -u.$$

2. Relation between  $\mu$  and  $h$  (velocity-constant),

$$h = \frac{\text{velocity of wave in air}}{\text{velocity in the medium}} = \frac{\sin r}{\sin i} = \frac{1}{\mu}.$$

3. Real and apparent depth.

The sagittae of the incident and refracted waves are in the ratio of  $1/h (= \mu)$ .

## 4. Position of focus of spherical mirror.

The sagitta of the reflected wave is twice that of the mirror surface, whence

$$V = 2R,$$

i.e.

$$1/v = 2/r,$$

and thus  $v = r/2$ , where  $v$  is the distance of the image from the plane wave (i.e. the focal length).

## § 5. UNIVERSAL FORMULAE FOR LENSES AND MIRRORS

This proof has manifest advantages over the one which makes use of certain rays. If the curvature of the incident wave from a distance  $u$  be called  $U$ , that of the emergent wave which will form an image at a distance  $v$  be called  $V$ , and the focal power of the lens be  $F$ , then

$$V = U + F.$$

Expressed as reciprocals this becomes

$$1/v = 1/u + 1/f,$$

whence

$$1/f = 1/v - 1/u.$$

In the case of mirrors, as in all reflections, the original curvature is reversed, and the focal curvature is then added:

$$V = -U + F,$$

whence

$$1/f = 1/v + 1/u.$$

The more advanced theory can be dealt with by similar means.

## § 6. THE PLACE FOR GEOMETRICAL OPTICS IN A SCHOOL COURSE

It is my considered opinion, based on my teaching experience, that not until the student has reached the point of understanding the principles of reflection and refraction, with applications, and the functions of lenses and mirrors, should geometrical optics be used. It then affords a most valuable revision of work done, serves to clarify ideas and is a help in relating the practical and theoretical work, but does not assume an importance that cannot be justified. The ray should be defined as "a line showing the direction of movement of an element of the wave-front," and it must be made quite clear that geometric lines of light have no existence.

## § 7. OTHER ITEMS OF THE CONTENT OF THE COURSE

The spectrum and colour. Complementary colours. Pigments. Colour matching and mixing. Achromatism. Sky colours. Rainbow. Invisible spectrum: ultra-violet, infra-red, radiant heat, "wireless."

Measurement of the velocity of light.

The eye and its structure. Peculiarities of normal and defective vision. Aids to vision. Optical instruments. Projection apparatus.

Sources of light. Efficiency. Measurement of intensity of light and illumination. Lumens and foot-candles.

Some reference to interference, diffraction and polarisation.

## § 8. DIFFICULTIES

These have proved less than might be anticipated. All pupils understood the basis of Huyghens' construction, which had been demonstrated by means of ripples. They enjoyed doing the diagrams. It is most important to let demonstrations with the tank and with light overlap, so that there shall be no danger of their being regarded as two unrelated series of phenomena.

With respect to the mathematics, the brighter pupils can cope with the "wave" proofs and enjoy doing them. For slower people it is probably wiser to limit one's teaching to the "geometric" proofs, which in any case should be given as alternatives. The main difficulty, and a serious one at that, arises over the question of sign convention.

## § 9. SIGN CONVENTION

The international convention of opticians agreed to call a converging lens positive and a diverging lens negative. Hence it is only reasonable to call the curvatures imprinted in each case by the corresponding sign. Thus light from an object reaching a lens is diverging and therefore negative, while light converging on a real focus is positive in sign. On reflection there is a reversal of curvature, and this is indicated by a change of sign.

On the other hand, in the teaching of geometrical optics, the only satisfactory method I have found is the one set out below, which follows naturally from the graph work done in algebra:

Always draw a diagram and consider the lens or mirror as situated at the intersection of the axes of a graph. Always place the object on the right-hand side of the lens or mirror, when  $u$  becomes positive, and allot a positive or negative sign to  $v$  according to whether the image comes on the right or left of the "origin" (as in algebraic graphs).

Thus it is seen that exactly opposite signs are obtained according to the method used, and of course this is a serious hindrance to teaching. I know of no way of overcoming the difficulty unless the opticians can be persuaded to change their nomenclature.

## § 10. GENERAL REMARKS

I am convinced, from my own experience, of the immense superiority, from the general cultural aspect, of the wave-concept approach to the study of light. The lessons were a joy to conduct, giving obvious pleasure to the students, and constantly stimulating their interest. Moreover, the ideas brought to the fore are essentially physical, and this aspect of the subject is not swamped under a flood of mathematical detail.

One other point deserves mention. It is most important in doing class experiments on light to use light and not pins. The latter may be less troublesome, but the value of experiments with pins is almost negligible in many cases, for the brighter pupils anticipate the results and the weaker ones never reach any. When beams of light are used even the quick workers find sufficient to hold their interest, and the slower ones are able to realise that optics is not such an unfathomable mystery after all.

## 9. GEOMETRICAL OPTICS FOR BEGINNERS

By L. MOORE, M.Sc., Leeds Grammar School

*ABSTRACT.* While the wave theory affords a useful means of revising geometrical optics it is not a suitable starting point. A pupil should use the same sign conventions throughout his school career; later, when more adaptable, he will not find much difficulty in making a change if that is found to be necessary. Experiments in which the images of luminous sources are projected on to screens by means of mirrors and lenses are to be preferred to experiments by the unconvincing pin methods.

### § 1. THE WAVE THEORY AS A STARTING POINT

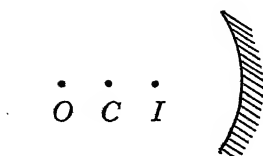
USUALLY not enough ground is covered in courses on elementary light, owing to the large amount of geometry introduced and to the numerous, but unconvincing, experiments by pin methods. There is a danger that the introduction of the wave theory at an early stage in the course might merely add alternative proofs of the mirror and lens formulae, and that even less ground might be covered than at present. If, however, the wave theory could be used to simplify and reduce the amount of geometry to be learnt and allow time to discuss interference, etc., the change would be welcome.

Prof. Silvanus P. Thompson adopted a method of teaching geometrical optics by means of the wave theory\*. If the method had proved successful, it would probably be in use to-day for beginners in optics. My own opinion is that while the wave theory affords a useful means of revising geometrical optics at the end of the higher school certificate course it is not a suitable starting point.

### § 2. SIGN CONVENTIONS

It is unfortunate that there are so many different sign conventions in use in text-books on light, and I believe that for the most part these are not the conventions used by opticians. Until I began to teach, the conventions I used were:

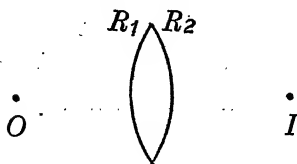
*Concave mirror formula*       $1/u + 1/v = 1/f = 2/R.$



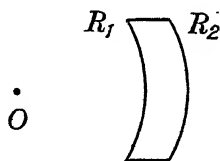
\* *Phil. Mag.* 38 (1), 232 (1889).

Convex lens formula

$$1/u + 1/v = 1/f = (n - 1) (1/R_1 + 1/R_2).$$



The formulae and the diagrams go together:  $u$ ,  $v$ , etc., are all positive. Changes in sign in the formulae are easily made.



$$1/u + 1/v = (n - 1) (-1/R_1 + 1/R_2),$$

where  $u$ ,  $v$ ,  $R_1$ ,  $R_2$ , etc., are again all positive.

If  $v$  works out to be negative, then  $I$  is on the same side as  $O$ .

There was very little difficulty in changing over to another system of sign conventions to secure uniformity in the school, and I believe that if any particular sign conventions be decided upon and used throughout the school years, the few students who continue to study optics will not find much difficulty in making a change later, if that is found to be necessary, for they will then be more developed and more adaptable.

### § 3. EXPERIMENTAL WORK

A series of class experiments is needed using (i) luminous sources and projecting their images on screens by means of lenses and mirrors; (ii) reflection and refraction of beams of light instead of the usual tracing of rays by sighting pins. Young boys could then carry out experiments such as the following:

(1) Use a convex lens to project on a screen the image of the filament of an electric lamp. Without moving the screen find another position for the lens so that the image is focussed on the screen. Explain by means of two diagrams the difference in the size of the image in the two cases.

The answer to this practical problem would be two diagrams and nothing else.

(2) Try to project on a screen the image of the filament of an electric lamp using a concave lens. Draw a diagram to show why you cannot succeed.



## 10. THE PLACE OF GEOMETRICAL OPTICS IN THE TEACHING OF LIGHT IN SCHOOLS

By H. TUNLEY, Merchant Taylors' School, Liverpool

**ABSTRACT.** A scheme is outlined for the treatment of light up to university scholarship standard. In this, geometrical optics has its customary prominent place. An argument is presented against its being displaced by a wave theory treatment, while its limitations can be indicated even to beginners. It is suggested that in the treatment of curved mirrors and thin lenses there is need for much simplification and rationalisation, but a drastic departure from traditional methods does not seem advisable. There is a considerable need for modernising the treatment of photometry in general. Up-to-date knowledge is not readily available and most textbooks are either out of date or misleading on this branch. A suggestion is made concerning the further treatment of light for the "scholarship boy."

**I**s there anything very much wrong with geometrical optics if properly presented? Is not the trouble largely due to muddled presentation and confusion as between teacher and teacher, textbook and textbook?

The elementary teaching of light can be dealt with under four main groupings founded upon:

- (1) Rectilinear propagation in a uniform medium.
- (2) "Laws" of regular reflection.
- (3) "Laws" of regular refraction.
- (4) Inverse square law.

Here we are dealing with facts—limited in application though some of them may be—which can be satisfactorily demonstrated even to the youngest student. The building of the structure on these foundations is an exercise of logical deduction which has, surely, a considerable cultural value.

By using a Hartl optical disc (or a similar appliance), the behaviour of a narrow pencil of light can be visually demonstrated, and the young student feels that he is dealing with realities—he can clearly conceive rays. Unless the student is older and has a good mathematical equipment before starting the subject, a wave theory presentation at the outset is not advisable. There is a difficulty in visualising a three-dimensional transverse wave, and by the time the teacher has been brought (by questions asked) to confess that "the ether may or may not exist but, anyway, we don't know anything about it and, moreover, these transverse waves are probably electro-magnetic in nature," the youthful mind is in a quandary and thinks it is dealing with unrealities. In the early stages a presentation based upon a theory is not as satisfactory as one based solely upon experimental facts and geometry.

If its limitations are carefully pointed out when opportunity arises, the method of geometrical optics is the more desirable treatment, and one, *par excellence*, in

which there will be nothing to unlearn later. If there is anything to unlearn it will be due to faulty presentation. Of the muddle that has arisen over the vexed question of signs we, in schools, are not entirely blameless, but first year university lecturers, and textbook writers are at least as much at fault. It is the experience of the author that geometrical optics can be presented without any great departure from the traditional methods, so that students have no difficulty over signs, and even on going through an honours physics course at a university, they find nothing to unlearn. This statement is made after due enquiries. Of the needs of the technical man the author is unaware, but is certain that, if by the time a student contemplates taking a post with a firm such as Ross's or Hilger's he is not independent of mere conventions and capable of quickly understanding a new outlook, then he is not able enough or "advanced" enough for the work. It is doubtful whether 1 in 1000 students of light in schools or 1 in 100 in the universities ever finds a career in technical optics, so that unless the technical man can expound to us a treatment of elementary optics as logical and simple as the present geometrical optics (properly presented) he must not expect from us more than a passing mention of his pet methods—even when we know what they are.

Appended are the mere outlines of a treatment of some parts of geometrical optics, but little of which may be original. It is not so much originality which is needed as careful systematic treatment. Inversion of an order or omission of an essential step makes all the difference.

#### APPENDIX

(1) *Rectilinear Propagation.* After shadows and eclipses have been satisfactorily dealt with the pin-hole camera is usually studied. This gives an opportunity to point out the limitations of rectilinear propagation. The pupil having suggested, as the result of "leading" questions, that decreasing the size of the hole will sharpen the image, it can be pointed out that there is a limit to this truth. This lesson can be followed up by the illustration, by experiment or photographs, of what happens to light from a narrow slit passing through a V-shaped slit. A suggestion to students to experiment at home with water ripples passing through variable gaps paves the way for an explanation by the wave theory later.

(2) "*Laws*" of reflection. Lecture demonstrations and measurements with an optical disc and individual experiments with apparatus such as Gallenkamp's optical ray apparatus, or that devised by Mr Meier of Rugby, will serve to convince the student of the truth of these so-called "laws."

There is much to be said for deducing all the well-known properties of plane and curved mirrors by simple mathematical steps from these laws and testing by experiment the results obtained at each step. This is rather a reversal of the method usually adopted in schools but it appeals to boys, if carefully done, and gives them confidence in the applications of mathematical methods to physics.

If the drawing of a caustic curve for the trace of a hemispherical surface precedes the usual study of spherical mirrors, the statement "the results hold only when the ratio *aperture/radius of curvature* is small" is fully comprehended.



$v = -3$ , say, which clearly brings the equation back to the right form for (2). Thus the student is convinced of the reasonableness and usefulness of the convention.

The author has also found it possible to simplify and rationalise the treatment of magnification, etc. without departing greatly from tradition.

As most higher schools certificate students know something of the properties of conic sections, the parabolic mirror should not be omitted.

(3) *Refraction*. Matters of apparent depth and total internal reflection present no difficulty, initially, to the ray treatment. Colour effects are noticed in the experimental work. Refraction through a prism leads to the observation that  $\mu$  is different for different colours and that the prism decomposes white light. Clearly, this cannot be deduced directly from the refraction "laws"—it is well just to hint at this stage that it can be explained on a wave theory, but to deal with it as an experimental fact.

Refraction through a lens can be treated via the thin prism or may be taken up after a preliminary treatment of refraction at a curved surface. It is of educational value to do both. Refraction at a curved surface should be treated in any case and the method should be similar to that for reflection using the approximation  $i = \mu r$  instead of  $i = r$ . This, then, presents no new difficulty to the student. Aplanatic foci should be emphasised. In proceeding in this way to the lens formulae the approximations introduced relative to aperture and thickness are made clear. The same sign convention has the same meaning and the same usefulness. After some general acquaintance with the properties of lenses the student has no difficulty in understanding that  $1/f$  measures the "power" of a lens or in realising why the technical man regards the converging lens as having positive power although the convention makes its focal length negative. He realises that positive and negative in these cases refer to two totally different conceptions—power to converge a beam in the one case and spatial position of the principal focus in the other.

Students find the sign convention a servant and not a hard task-master—it is often more useful and less confusing than some of the ingenious schemes for avoiding it.

The "thin prism" method of approach, which should certainly be given to higher school certificate students in addition to the above, yields, at an intermediate step (at least by Dr Searle's well-known method), the important relation that  $\delta = h(\mu - 1)(1/r_2 - 1/r_1)$ , where  $\delta$  is the deviation,  $h$  is the perpendicular distance from the axis at which the ray passes through the thin lens and the sign convention is used. This leads to a possible method for tracing the path of a ray through a system of thin lenses.

At this stage the following point of view, for which the author is indebted to Assoc. Prof. J. Rice, has interest and value:

$1/f$  measures the power of the lens to cause convergence.

$1/u$  measures the divergence of the incident beam.

(Divergence of inc. beam) — (convergence due to lens) = (remaining divergence),

i.e.  $1/u - 1/f = 1/v$ .

If  $1/f > 1/u$  then the remaining divergence is clearly negative, a fact which signifies "convergence." Similar considerations apply to diverging lenses. This outlook is quite independent of our previous convention of signs. If taken earlier, instead of the treatment previously given, it scarcely brings out the limitations of the thin lens theory and so has not the same educational value.

When will examiners and textbook writers cease grouping lenses as "convex" and "concave" and adopt the more rational "converging" and "diverging" grouping?

With regard to optical instruments only the elementary principles can be given in schools and university first-year courses. In telescopes, for example, the reason for long focus object glass and short focus (high power) eyepiece can be given, correction for chromatic aberration can be dealt with fully and spherical aberration to some extent. A mention that there is no advantage in increasing the power of an eyepiece beyond a certain value and that there is great advantage in increasing the aperture of the objective joins with the remarks arising from the pin-hole camera in preparing the mind for future work.

(4) *Inverse square law.* There is need for drastic modernising of the teaching in this grouping. The teaching must deal with a unit standard source of light and two derived units—the unit of luminous flux (the lumen) and the unit of "illumination" (foot-candle or metre-candle) and the relation between these.

Mean horizontal and mean spherical candle-powers should be introduced.

In photometry we still meet—even in new textbooks—the instruction to adjust so that the "grease spot may *disappear*" on both sides at the same time! Moreover, the inverse square law is stated "for a point source" and then, all too frequently, used in photometry where the sources are by no means points without the slightest reference to errors introduced if the distance from source to photometer is small. The "ten times" rule used in accurate photometry should be known. Many serious students have been worried by this trouble.

Few textbooks mention the above units (i.e. the lumen, etc.) and many teachers may be unfamiliar with them. Those textbooks which do mention them usually give unnecessarily complicated definitions and introduce unnecessary units such as the "lux."

The author would like information as to the best way to present the unit standard source of light. Supposing we say a unit source is a point source of unit candle-power radiating uniformly in all directions; some such definition seems necessary in order to present the "lumen" satisfactorily, but how is it best stated in terms of a fundamental standard? Is the fundamental standard in this country still the pentane lamp? Can the above standard be stated as such that if ten be grouped together they would emit per second per unit solid angle the same quantity of light as is emitted per unit solid angle per second in a forward direction by the pentane lamp?

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The "scholarship boy" can be introduced, firstly by experiment (colours of thin films, etc.), to the whole range of optical phenomena which come outside the

above four groupings. That all these facts can be satisfactorily correlated if light be regarded as wave motion gives sufficient incentive for a close study of wave motion, and by this time the student is mathematically equipped to tackle it satisfactorily. A return should then be made to elementary facts to show that the assumption of wave motion is not inconsistent with the "laws" of reflection and refraction. The student should be warned that such a simple wave hypothesis cannot account for many facts concerned with absorption and emission, so that it probably represents only one incomplete aspect of the truth.

## II. THE TEACHING OF GEOMETRICAL OPTICS BY MEANS OF THE GAUSS SYSTEM WITH SPECIAL REFERENCE TO THE FORMATION OF IMAGES

By CONRAD BECK

*ABSTRACT.* The teaching of optics should be based upon the principles of image formation treated according to the Gauss system, the nature of the approximations which are involved being duly explained. The Cartesian convention as to signs should be applied, with the origin at a suitable fixed point in the system while the light is always considered to come from the left. No convention should be used in which the signs change with the nature of the lens.

I CONFINE my remarks on elementary optical education to that branch of the subject which covers lenses and optical instruments composed mainly of lenses. The teaching of physical optics is of course equally important, and it is assumed that the principles of refraction, reflection, interference, diffraction and polarised light have been taught in an elementary manner.

I strongly recommend that the geometric principles of dioptric instruments should be taught by means of rays and not by wave-fronts. I have not yet seen a system dealing with the subject by means of wave-fronts which lends itself to the explanation of the formation of images by lenses and lens systems. Many years ago I studied the ordinary Cambridge text-books of those days—Parkinson—Heath—Hermann, etc., and it was not till I read a German book on the Gauss theory that I ever obtained a mental picture of the action of a lens system. It may be that a system equally simple and equally illuminating could be devised in which the wave-front method is employed, but until that has been done I strongly urge that lenses should be treated with special reference to the formation of images, and that the subject should be treated by the Gauss system. This system is of course based on approximations which must be clearly explained, and it must be understood that the theory is only an imperfect hypothesis. It can, however, be applied without sensible errors to so many optical instruments that it is invaluable for presenting to the student a concise description of the action of an optical instrument.

The following characteristics can be dealt with: Position and sizes of images. Magnifying power. Illumination and photometry. Entrance and exit pupils. Field of view. Aperture. Working distance. Perspective.

I suggest that simple lenses should be considered on three methods with special reference to the formation of an image:

- (1) The images of points on the axis of the lens.
- (2) The direction of several axes of oblique bundles incident from selected points on an object which are not on the axis.
- (3) The consideration of one complete bundle of light from a point on an object some considerable distance from the axis.

Combinations of lenses should then be considered on the same three methods, and these methods should be applied to at least six typical optical instruments to find the optical characteristics of such instruments. Achromatism can be roughly worked out by the Gauss theory, and then, but not till then, aberrations and the general principles of their corrections should be explained. Their correction by calculation, except in the case of achromatism, should not be attempted in any elementary education.

The analytical and geometric work must be done on a reasonable convention as regards signs. Light should always be considered as coming from left to right. Distances to the left of the origin should be minus, to the right, plus. North should be plus and south minus. The origin should be the non-variable point and in general this is the vertex of the refracting surface or the equivalent plane. If the equivalent planes are separated their separation is plus, and if they are crossed it is minus. No system of signs should ever be used in which the convention as to signs change according to the nature of the lens or optical system. Such systems lead to infinite trouble.

For a complete description of this method of reckoning signs, I would refer to Ferraris on *Dioptric Instruments*\*.

The problems of reflection can be treated by means of dioptric formulae if  $\mu$  be considered as equal to  $-1$ , but the question whether this device would work out conveniently for general purposes would require some consideration on account of the reversal of the direction of the light.

I consider that the Gauss system is of such value in giving rational understanding of lenses that I should propose teaching the general case first and taking the thin lens as a special case where the equivalent planes coincide and teaching both the principal and nodal planes, and taking the lens with air on each side when the combined nodal and principal planes become the equivalent planes as another special case.

There are certain general ideas that require special attention in the above teaching. It is important for the student to understand that rays of light and points are not geometrical lines and points but are only used as a means of finding positions. The limitations of the Gauss theory should be thoroughly recognised, and the conditions under which they can be suitably applied should be understood.

I do not consider that elementary education should be purely experimental as advocated by Mr T. Smith. If no analytical method were available, except one requiring advanced mathematics, there might be something to be said for such a plan, but algebra and a very slight knowledge of trigonometry are sufficient for the treatment of image formation by the eye and most optical instruments; and it is the proper appreciation of the principles of image formation that should form the basis of general optical education. The special work on the correction of aberration and the details of the design of instruments is only required by a few specialists and cannot form a part of elementary education.

\* Faber, H.M. Stationery Office.



## 12. GEOMETRICAL OPTICS AT THE NEWER UNIVERSITIES

By W. EWART WILLIAMS, M.Sc., King's College, London

*ABSTRACT.* The various grades of geometrical optics teaching at King's College, London, are briefly outlined. Experience has shown the Abbé method, as developed in Drude's *Optics*, to be the most instructive method for both the special and general honours courses. It is suggested that the Physical Society should set up a representative committee to select a system of sign convention and notation and press for its general adoption.

IT is with considerable diffidence that I yield to the persuasions of the assiduous Hon. Secretary of the Physical Society to make a contribution on this subject; it is only the realisation that I have spent several years on the industrial as well as the academic side of optics that has finally persuaded me to write these notes.

The following remarks refer in particular to the undergraduate teaching at King's College, London, but are probably applicable in general to the majority of the newer universities. We have to recognise three separate grades or standards of study:

### § 1. SPECIAL HONOURS COURSE

(A) Honours B.Sc. (special honours course at the University of London).

(B) Pass B.Sc. (general honours, the University of London).

(C) Intermediate (including 1st M.B. and Conjoint Board Examination).

If the dovetailing of these separate courses can be improved and a uniform system of notation and sign convention be adopted, this discussion by the Physical Society will not have been in vain.

Considering first of all the geometrical optics teaching in the *A* class, it is an unfortunate fact of which no one will be more conscious than myself, that the student after completing the course is not able to carry out lens computations and would apparently be useless in the lens designing department of an optical factory. It is probably this fact that has given rise to the discussion. Many will have heard the complaint of the universities' failure in this respect. It comes mainly from those manufacturers who expect to have a plentiful, and therefore eventually cheap, supply of optical designers. The old reproach of Lummer and S. P. Thompson that geometrical optics was a mere side line of mathematics is no longer true. We no longer find examination questions that only require a knowledge of Snell's law and a certain amount of ability in algebraic and trigonometrical transformations. The problems of the rainbow are left entirely to the mathematics classes.

The real source of the trouble is that in preparation for an honours degree in physics, only a very limited amount of time can be allocated to geometrical optics. In fairness to the students, the lectures and practical work in the different branches

have to be divided according to the relative importance attached to them as shown by the examination questions. There is as far as I can see no reason for thinking the present division unfair, but as measured from the examination papers of London University, the whole of "light" only represents one-fifth of the two years' (post-intermediate) course. Geometrical optics is represented by about one quarter of this, the remainder being physical optics and including the electronic theory of dispersion and series spectra. *The selection of questions is such that a candidate can obtain full marks without attempting any geometrical optics questions.*

It is obvious that if a student is to be of immediate use in an optical workshop his training must be much more extensive. He could profitably spend the whole of the two years on geometrical optics together with the necessary subsidiary mathematics. On the other hand, if such courses were generally available at our universities I doubt if we should have the students, for the opportunities of suitably placing them afterwards would be very few. The only student that I have had during the last nine years who has shown a particular liking and aptitude for this subject, and who, for pure interest, has subsequently followed it up in considerable detail, is now engaged in an electrical laboratory. I failed to find a suitable opening for him in the lens computing work that he preferred.

The needs of the industrial world must be fully satisfied by the supply from the Applied Optics Department of the Imperial College, where the subject is studied by itself and not as a very small branch of physics.

In the short time available the best course, in my opinion, is to follow the treatment of Abbé's theory as given in Drude's well-known text-book. The student's grasp of the subject should be checked by letting him calculate the equivalent focal lengths and the positions of the cardinal points for actual doublets as well as for the "examinational" hemisphere immersed in oil tanks, etc. Practical work on a photographic objective, with the use of Dr Searle's instructive apparatus, helps considerably in consolidating the theoretical work. No systematic analysis of aberration (other than chromatic) is made, but the importance of the sine law and the effects of apertures are emphasized. In this connection I would like to mention that a few weeks ago I was examining a special instrument, the optical parts of which were made by a well-known British optical firm. In order that it might be used successfully, the illuminating lamp had to be so overrun that it had a life of a few hours only, yet the numerical aperture of the system used was comparatively low.

Finally the adjustments of a spectrometer are carefully considered; this is especially needed because no adequate treatment is given in any of the usual text-books. Practical work with an accurate spectrometer that is put out of adjustment before the student begins to use it is very useful in this connection, provided that only correspondingly accurate results be accepted. The training thus gained is of value throughout the whole of physics.

It would be interesting to study the defects of images in more detail, for example along the lines of Prof. Whittaker's delightful monograph in the Cambridge Mathematical Tracts, but with the time available this is not possible. I believe it is better to concentrate on first order theory as outlined than to aim at a necessarily scrappy

general picture of the whole subject. The student entering an optical workshop has nothing to "unlearn" and his familiarity with first-order work will always stand him in good stead. I would mention here that until some further generalisations have been made in lens theory the real practical work of lens computing will not be materially lessened.

## § 2. GENERAL HONOURS COURSE

These students are expected to understand the essential properties of thick lenses and the significance of cardinal points, etc. During the last few years I have experimented with the various ways of presenting the subject. The most successful method, involving the least amount of pure memory work for the student, has proved to be a simplified form of Abbé's theory. The collinearity equations (in two dimensions) are derived by trial from the easily accepted facts that only one point image of a single point object is required and that the image co-ordinate must be finite (at the focus) when the object is at infinity.

In dealing with nodal points it seems well worth while to demonstrate the reality of their existence and their properties. This is simply done by placing a blackened slide, on which a cross mark has been scratched, in the lantern and adjusting the objective so that the slide is at its focal plane. An aerial camera lens of about 1 metre focal length is placed on a turn-table and the image is formed on a small screen. The absence of any displacement when the lens is rotated about the nodal point (obviously not the centre of the system) is very striking, and can be shown to a large class by substituting a suitable objective for the hand screen and projecting the image on to the wall.

Apart from a descriptive account of the aberrations (chromatic aberration is studied in more detail) this, together with a brief outline of the chief optical instruments, is all that can be covered in the time. An additional advantage of this method, that was not foreseen at the beginning, is that several students who complete their general honours course in two years spend their third year in special honours work. The continuity of treatment thus effected is of great benefit to them not only in consolidating their earlier work, but in giving them more time for further individual study.

## § 3. INTERMEDIATE COURSE

The only comment I wish to make with regard to the intermediate and the corresponding higher school stage is this. For the sake of those students who may be studying the subject further, the sign convention should be altered so that it is in agreement with that used in their later studies. I have seen many examples of the confusion due to the change, and well remember my own difficulties in reading a now classical English treatise on the subject, due merely to the unique convention adopted in it.

The convention that we use is to consider a surface positive if convex towards the object, while distances of object and image are positive if they lie on the lens side of their corresponding focal points, which serve as origins. To keep the usual

intermediate convention would needlessly complicate the higher work while no standard reference book using that notation would be available for consultation by the student.

In conclusion I would venture to make the following constructive suggestions:

(a) That the examination papers in optics should be so amended that full marks cannot be obtained without attempting some geometrical optics questions.

(b) That the Physical Society, in connection with representatives from other interested bodies, should set up a committee to devise a new, or select an old system of notation and sign convention, and press for its general adoption.

## 13. A COURSE IN GEOMETRICAL OPTICS

By G. C. STEWARD, M.A., D.Sc., University College of Hull

*ABSTRACT.* Geometrical optics is at present out of favour as a subject for university teaching. In this paper a suggested course in geometrical optics is given, embracing the elementary non-aberration part of the subject and based upon the Newtonian formula  $xx' = -ff'$  and the idea of geometrical collineation; together with a presentation of the more advanced theory, based upon the characteristic function of Hamilton or upon a modification of this function. Suggestions are also made for bridging the present-day gulf between theory and industry.

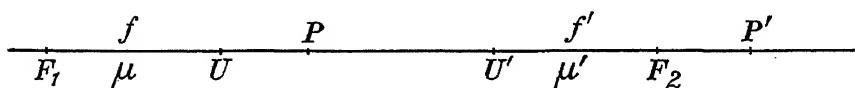
THE subject of optics, in its geometrical aspect, has been studied from early times, and that this should be so is natural since light plays so important a part in man's experience of the natural world. And since the seventeenth century, perhaps, the subject has been peculiarly English; over a considerable period of time English glass and English lenses and mirrors held a high reputation, and it is only in comparatively recent times that this country has been subject to foreign dominance in optical matters. Moreover the theory of optical systems was investigated here quite early, and a number of results were obtained and mathematical expressions discovered by English writers—results which now commonly bear other names; for example, the Petzval sum and four, at any rate, of the five aberrations of von Seidel were discovered by Airy and Coddington before the time of Petzval and von Seidel. It is natural therefore that the more theoretical side of geometrical optics should have received some considerable attention, and it follows that the subject, in its more elementary parts, has been worked out somewhat extensively. And partly in consequence of this geometrical optics is largely out of fashion in our day in English universities; but also several other reasons operate to this end. The subject appears isolated—it does not seem at first sight to stand in any close relationship to other branches of mathematical or physical enquiry; the elementary theory of systems of lenses and of the bending of rays of light in their passage through various optical media—all this appears an out-of-the-way subject and removed from the high road to any wide scheme of mathematical or physical education. And further it must be admitted freely that the common method of presentation in academic circles is too often not attractive; for one thing perhaps there is not sufficient contact with practical work, with the handling and use of optical apparatus in the laboratory: and, too, not a few teachers are themselves wholly uninterested in the subject, regarding it merely from the point of view of giving to their students the minimum amount for examination purposes. The consequence of all this is that geometrical optics is ejected from the syllabuses of university examinations whenever possible.

In the present discussion it would seem useful to consider two matters and, in the first place, to consider them separately; namely, geometrical optics as an academic subject studied by reason of its own interest and, it may be added, from the point of view of examinations, and, secondly, as an industrial subject—as carried out in the actual design and manufacture of optical systems. And there falls also to be considered the very definite and wide gulf which separates these two at present, so that we may find if possible some means of bridging the gap. As regards industrial methods in geometrical optics—the various ways in use of computing and designing optical systems (and I understand that these are very highly individual)—I cannot claim very close acquaintance with many of them; although I have done my best to keep myself informed of as many of these methods as may be, and of the practical bearing of optical problems.

With respect to the academic teaching of geometrical optics whether elementary or more advanced (although for the most part as far as I am aware it is almost wholly elementary) it must be admitted that the subject as commonly encountered in the text-books is not attractive—in the form of repeated applications of the formula  $\pm 1/v \pm 1/u = \pm 1/f$ , the signs of these quantities being (to me) to the last degree uncertain and puzzling. And, inasmuch as the student, at present, is unlikely to pursue geometrical optics in its higher branches, the more fundamental principles of the subject do not ever appear to him. The thing which strikes one in contemplating so many presentations of elementary optics (and by elementary optics here is meant a treatment which neglects the theory of aberrations) is the continued necessity for approximation and the (to me) completely baffling sign conventions which are adopted. Approximation of course there must be if one is to neglect aberrations; but it would appear possible to acknowledge this initially and to realise then that one is dealing with a system of purely geometrical collineation—with a unique one-to-one correspondence, that is to say, between the points, lines and planes of two three-dimensional regions which may be labelled, for the sake of importing optics, the object space and the image space respectively. It is not suggested that the first approach to geometrical optics should be after this manner, whether for the mathematical or for the non-mathematical student; but this view of elementary optics is perhaps the one to which the student should be led eventually. The introduction to the subject might well be made through practical work so that the student learns from the handling and use of lenses and lens-systems in a laboratory that he is dealing with a real subject in the natural world; he should begin here so that he may keep this in mind in his subsequent study of the subject. But the time ought eventually to come when he studies the pure theory of geometrical optics, and it would appear to be a gain—for the more mathematical student certainly and I think for others too—if he realises that in the elementary theory he is dealing purely with a geometrical collineation.

In teaching elementary geometrical optics to undergraduates reading for the Tripos at Cambridge, and elsewhere, I have always aimed at an early exposition of the Newtonian formula  $xx' = -ff'$ , the principal foci of course being the origins of co-ordinates; together with the associated results  $x = f/m$  and  $x' = -mf'$ , the

notation being as usual. For mathematical students these results are almost intuitive, but for such students, and also for others having less of a mathematical equipment, I have first worked out various simple problems involving thin lenses and mirrors, seeking always, however, to reach the above results, in the first place as particular cases but finally as a general law for all optical systems; emphasizing at the same time the fundamental character of the formulae and showing carefully that they include all cases which can arise in a consideration of the elementary, non-aberration, properties of the symmetrical optical system composed of lenses and mirrors or of any combination of these. This implies the introduction of the idea of cardinal points and cardinal planes—due to Gauss—in the first place gradually and for particular systems, but finally, and for mathematical students perhaps immediately, in the most general manner; so that the student may learn to regard any particular system as but a special case of the general system. From a knowledge of the positions of any two of the three pairs of cardinal points, namely, the principal foci, the unit points and the nodal points, the solution is of course immediate for any non-aberration problem concerning a symmetrical system. Thus if one finds for example the positions of the principal foci,  $F_1$  and  $F_2$ , and of the unit points  $U$  and  $U'$ ,



then since by definition  $F_1U \equiv f$ , the first focal length of the system, and  $U'F_2 \equiv f'$ , the second focal length of the system, one can find the axial point  $P'$  conjugate to any given axial point  $P$  by means of the result

$$F_1P \cdot F_2P' = -F_1U \cdot U'F_2,$$

and the magnification associated with these points from the relations

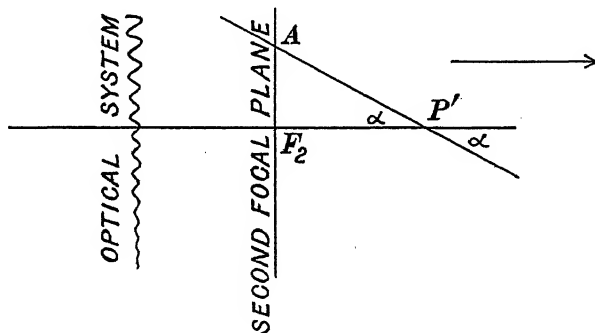
$$F_1P = F_1U/m \quad \text{and} \quad F_2P' = -mU'F_2.$$

For the general optical case this implies an ability to find readily the positions of  $F_1$ ,  $F_2$ ,  $U$  and  $U'$ ; and the method is first to write down the power ( $K$ ) of the system and then the positions of  $F_1$  and  $F_2$  relative to the first and last optical surface respectively, using for this purpose the results already obtained; while finally  $U$  and  $U'$  may be fixed in position by means of the result  $f/f' = F_1U/U'F_2 = \mu/\mu'$ ,  $\mu$  and  $\mu'$  being the optical indices of the end media respectively.

In simple problems involving only two or three refracting surfaces the various formulae can be obtained once for all and quoted as required; but they are so obviously special cases of the general results for any number of surfaces and these general formulae are so compact and easy to remember that it appears to me to be well worth while to give them to the student after a suitable introduction, so as not to leave him only with special cases. And here a word may be said about the use of continued fractions; for the consideration of the general case, involving any number of reflecting or refracting surfaces, continued fractions offer a very

obvious convenience and they can be introduced quite simply even to elementary students. For one thing, only the barest elements are necessary, and I have found that they can be explained *ab initio* as they are required; and the increase in, and feeling for, generality so acquired is I feel of quite definite value. Further, and this applies to students who are to pursue the subject in its more advanced branches, whether academically or from the industrial point of view, the methods lead to a simple way of computing the general system and also its aberration coefficients to be mentioned later. And finally after reaching this general view of the elementary parts of the subject I have commonly taken a large number of examples as problems, whether very simple or more complicated, and have worked them out, or caused the students to work them out, showing that this may for all cases be effected quite simply by the one general method.

A word may be added here perhaps as regards the sign convention adopted; which is that all distances whatsoever are regarded as positive when measured in the direction in which light is travelling through the system. This will imply that angles are regarded as positive when measured as in the following figure:



$F_2P'$  is regarded as positive and also the angle  $F_2P'A$ .

In conclusion of this part of my subject, and indeed with reference to what follows, I may be permitted to mention a book\* of my own recently published, in the first chapter of which is given an outline of the theory of the symmetrical optical system from the non-aberration point of view. The outline is of necessity highly condensed since the book in question attempts to give an outline theory of the symmetrical system both as regards the geometrical aberrations of the several orders, and their computation, and also the effects of these aberrations upon the diffraction patterns associated with the system; and all this in small compass. But I have constantly used the general methods, suitably amplified, for first year students; and these methods have been designed too as an introduction to the higher branches of the subject.

The interest of geometrical optics, however, whether from the academic or from the industrial point of view, lies in the discovery and use of general principles and in the discussion of the actual behaviour of optical systems as contrasted with

\* *The Symmetrical Optical System*. Cambridge Math. Tracts, No. 25.



the idealised behaviour of the perfect system presented above; in a word in the aberrations of the system. A general method of investigating these is necessary, and we must also keep in mind the diffraction patterns associated with the optical system and their modifications in the presence of the geometrical aberrations. We are led at once to the wave theory of light, to which, I feel, the student cannot be introduced too early. Not a few of the elementary, non-aberration, properties of the system can be obtained directly from the wave theory, for example, the deduction of the two principal foci and focal lengths and the relation  $f/f' = \mu/\mu'^*$ . And it is a gain if the student is taught at an early stage to think of wave surfaces and of the rays of light as being merely normals to these surfaces.

We are familiar with the present-day ideas of quanta in connection with energy propagation and in particular in connection with the propagation of light, but we believe that these quanta have waves associated with them—waves obeying the general laws of wave propagation. The synthesis of these theories is yet to come—or perhaps is now coming through the new wave mechanics; but for a general point of view in geometrical optics we may fall back upon the wave theory. And the student finds intuitively evident the constancy, for a path variation, of the length of the optical path between two accurately conjugate foci, when he visualises waves expanding from the one and contracting to the other after successive reflections or refractions. Further, the mere idea of waves, combined with the conception of interference, leads at once to the idea of a unique geometrical path for a ray of light between two arbitrarily assigned points, through the intervening optical media; that, namely, for which neighbouring paths interfere least, or that for which the number of wave-lengths is stationary for a slight variation of geometrical path. Hence at once the principle of the stationary path between two points  $P$  and  $Q$ , in the usual notation,

$$\delta \sum_P^Q \mu \delta s = 0 \quad \text{or} \quad \delta \int_P^Q \mu ds = 0,$$

where  $\mu$  is the optical index, proportional to the reciprocal of the wave velocity, for the medium in which the element of path  $\delta s$  is measured; and the symbol  $\delta$  denotes an arbitrary, small, variation of the geometrical path between the end points  $P$  and  $Q$ , which themselves remain fixed.

I do not think that any elaborate apparatus or mathematical knowledge is necessary to give the student a clear understanding of this principle which is purely physical in origin and character; and the simple elementary results for an optical system may be obtained readily from an application of it while of course the general theory may be obtained from it immediately.

Sir William Hamilton embodied this principle in his characteristic function and in the several modifications which he gave of this function, including that one now known as the Eikonal and associated with the name of a subsequent investigator, Bruns. It was pointed out by the late Lord Rayleigh how readily an examination may be made of the first order aberrations of the symmetrical optical system (and equally one may add of the aberrations of any order) by means of this

\* Cf. *The Symmetrical Optical System*, Ch. II, § 3.

characteristic function; and other writers too have dealt with this point of view, for example, Clerk Maxwell, Larmor, Bromwich, T. Smith, etc. It is not my province to enter here into details of the application of the characteristic function or of the eikonal; I may perhaps refer again to the book mentioned before where a connected account of these matters is given. It will be sufficient simply to say that by an expansion of either of these functions in terms of suitably chosen variables (and a great deal lies in a suitable choice of variable) an examination of the geometrical aberrations may be made quite readily, and the nature of each of them investigated, for aberrations of any and all orders. The general method is to evaluate, for example, the eikonal for a hypothetical system, supposed perfect, that is, free from aberrations for two conjugate planes at a given magnification  $m$ , and then to evaluate it for the general optical system; the difference between these two results, named the aberration function and introduced by T. Smith, sums up in itself all the aberrations of the system and depends upon these aberrations alone. We have here a compact, ready and convenient method of investigating the qualitative and also the quantitative nature of the geometrical aberrations of all orders; from the practical and industrial point of view it is necessary of course to consider them quantitatively, and this too may be effected by means of the aberration function; it is here perhaps that we may bridge the present-day gap between theory and practice. We find formulae giving the aberrations of a single surface and then further addition formulae to give the effect of the addition of several surfaces; in this way obtaining the total aberration effect of a combined system in terms of the separate effects of the several components of the system.

And finally there remain the problems concerning the diffraction patterns associated with optical systems and their modification in the presence of the geometrical aberrations; these again may be investigated very readily by means of the characteristic function. A more elaborate mathematical equipment is necessary here if the problem is to be examined in its generality; although some progress may be made through numerical quadratures of the integral expressions obtained. But for an outline of this I may refer again to the book already mentioned and to the references given there.

The preceding gives a very brief outline of the method which I have adopted in teaching students the more advanced parts of the subject of geometrical optics; and I think that I can say that the students have been interested in the presentation.

## 14. OPTICS IN THE INDUSTRY

BY JAMES WEIR FRENCH, D.Sc., F.INST.P.

*ABSTRACT.* The subject is discussed only from the industrial point of view. The first point raised is that educational authorities cannot subordinate more important interests, such as those of the chemical and electrical industries, to the minor claims of the optical industry which, although important, is comparatively small. A statement of the needs of the industry leads to the second point, that, as the work of an optical designer so largely depends upon his workshop and general experience, his training must come from the industry itself, and that only a good, comprehensive education including a knowledge of fundamental optical principles is necessary as a preliminary to workshop training.

**I** TAKE it that the purpose of this discussion is to outline a course of optical study that will be of general educational value, that will be of service to the industry, and that will help the user of instruments to appreciate their optical performance.

From the industrial point of view, I should prefer to consider first what type of education best suits our requirements. Before doing so, I cannot refrain from suggesting that difficulty must be experienced, not so much in the formulation of a course of study as in the reformation of what exists, since such reformation must involve an increase in the number of lecture hours.

Here and there throughout the country some individual teaching of optics may be found, but in general it forms no important part of a school curriculum. If we exclude the admirable practical teaching of Prof. Conrady at the Imperial College and the ophthalmic teaching at the Northampton Institute, the subject of optics—other than physical optics suitable for examination purposes—forms a very small part of the teaching of our colleges and universities. Our physicists and mathematicians are not disposed to devote their time to the material aspects of optics. All who can do so are more profitably employed groping among the ruins of the 19th-century edifice of science, searching for the architect's plan and building new foundations here and there where the ground seems reasonably sound, hoping to find a ray of light among the débris.

Educational authorities would no doubt be very willing to teach everything well, if circumstances permitted. But they are unable to do so. From all sides they are pressed to allocate more hours of study to cope with the rapid development of chemical engineering and the electrical industry. Three-year courses have been extended to four and hitherto essential subjects have become alternatives. Reformation of optical teaching means an extension of hours and, when one considers the strength of other appeals, it is difficult to know how these can be allocated, either in schools or colleges.

My first point is that educational authorities cannot subordinate more important interests to the minor claims of the optical industry which, although a key industry, is a comparatively small one.

It may help us to form some idea of the kind of optical instruction which is desirable if I outline the work involved in the design of an optical instrument. In small concerns such design may depend upon the enthusiasm of an individual of

outstanding ability and ingenuity. To an ordinary mind computation work can be appallingly monotonous and there are many men who, having the other qualifications, fail in this particular respect. Such an individualistic system is only of limited application. In larger establishments the individual must be supported by a number of assistants. I recollect that, in the case of one important continental firm, the material prepared by one individual was handed over to about thirty or forty computers, expert in the use of logarithmic tables but otherwise of no very special education. This was before the introduction of computing machines which have reduced so materially the actual labour of calculation. The design of an optical instrument is not the work of such computers. The actual designer may not be skilled in this particular section of the work, for the reason that the mechanical may dominate the optical. When the optical system as a whole has been designed, the computation of the elements, individually and in combination, is entrusted to the operators of the calculating machines who need have no exceptional mathematical equipment other than a common knowledge of the simple trigonometrical expressions, which can hardly be regarded as mathematics. Particular rays are traced step by step through surface after surface for the purpose of determining at various stages the longitudinal and transverse aberrations. These values are assessed by the skilled computer who decides at what particular part of the system a modification can best be effected. His special skill is much more practical than mathematical. It is based essentially upon industrial and commercial experience that can be gained only from years of active practice within the industry itself. It depends upon a knowledge of what is necessary to excel the productions of progressive competitors. It involves experience of workshop conditions and, above all, good judgment in the balancing of one type of aberration against another, for no optical system can be free from all kinds of aberration. To satisfy the needs of some particular client, it may even be necessary to re-assess the relative importances of the various aberrations to suit the ideas of the customer.

Some particulars regarding a typical submarine periscope of average dimensions will afford an indication of the magnitude of the work involved in the computation of the optical system. Of simple operations involving, say, two multiplications and one division, there are 12,000 in this particular example, which is not an extreme case; the number of individual operations is about 40,000; and the amount of writing involved is equivalent to the writing of a 70,000 word book. When it is considered that the instrument in question has to be designed and constructed within the limits of a contract date with the probability of a penalty for delay in delivery, it will be realised that in actual practice such work cannot be undertaken by an individual; it must be so organised that it can be distributed over a group of computers.

So far as the general design is concerned, methods no doubt vary greatly. My own particular system is somewhat as follows. The most suitable way of meeting the specification having been decided upon, an optical diagram showing the positions of the lenses, the central beam, and the oblique beam, is prepared; this path-in-air diagram is adjusted to suit the principal rays determining the angular field and the cones of rays determining the illuminations at the centre of the field

and at the margin. Upon this diagram the thicknesses of glass are then indicated and the diagram is adjusted accordingly, the amount of adjustment generally being small as, with experience, allowance can usually be made in the initial diagram for the air/glass differences. The principal thicknesses having been determined, the system is redrawn with greater precision, the final dimensions being checked by calculations, all of the simplest arithmetical kind. The designer knows from experience the difficulty that may be incurred in the computation of each particular element and his principal aim is to ensure that he does not set the computers too difficult a task in any one respect. There is great scope for ingenuity in the preparation of this original design and it is in this particular stage that the most effective work is done. Particulars of the system are then sent to the computer. He receives information regarding the focal lengths and diameters of the various elements, approximate thicknesses of the lenses and prisms, and air separations. He also receives for the axial beam its radius at the entrance surface of each element and for the extreme oblique beam the radial distances of the points of intersection of the principal ray with the respective surfaces. The approximate radii of the individual surfaces of each combination are then calculated by simple proportion from some existing similar combination; it is rarely necessary to compute the curves *de novo*, but even if that were necessary the ordinary simple approximate formulae would suffice for the purpose. The approximate curvatures having been determined, the work of computation by the now well-known trigonometrical system can then be commenced.

Practical considerations then determine the progress of the work. Theoretically it may seem desirable to modify the surfaces of one of the large diameter objectives or projectors. This, however, would involve the construction of large and expensive test plates. Practical considerations make it advisable to manipulate the smaller diameter entrance or exit systems.

My second point, therefore, is that the work of an optical designer so largely depends upon his workshop and general experience that his training must come from the industry itself and that only a good comprehensive education, including a knowledge of fundamental optical principles, is necessary as a preliminary to his workshop training. A schoolboy's education must of necessity be general, as the kind of work he will be engaged upon later is quite unknown. The more determined he is to become an optician, the likelier he is to become something else. Of the hundreds of boys of whom I have had experience, I cannot remember one who possessed more fundamental knowledge of optics than could be acquired by him in a few evenings of purposeful study. And so far as the kind of optical knowledge required by the industry is concerned, the same applies to graduates. I personally have long since ceased to expect any such specialised knowledge. I prefer to remember that inherent qualities may be of more permanent value than those acquired, that the steel industry was revolutionised by a clerk, that after the Fire of London an optician was entrusted with the design of St Paul's, that James Watt—another optician and instrument-maker—became the greatest of steam engineers, and that on the other hand we owe the art and practice of optical glass making to a carver of clock-cases.

## 15. THE NEED FOR MEETING PRACTICAL REQUIREMENTS

BY INSTRUCTOR-CAPTAIN T. Y. BAKER, F.INST.P., R.N.

**ABSTRACT.** The subject should be taught so as to be of use both to users of optical instruments and also to designers. The course should be mainly Gaussian optics with only a qualitative exposition of aberrations. Much more design work of a Gaussian character ought to be done, particularly with the view of ensuring requisite diameters to lenses. Examples of optical systems should include more modern instruments and not be virtually confined to the astronomical telescope. There is scope for a far greater development of the analysis and design of reflecting prism systems.

**O**PTICS, like many other branches of applied physics, leads to a definite technical end, the designing of optical instruments. In teaching the subject, sight must never be lost of the needs of the professional designer. At the same time—as in other subjects—optics is of deep interest to the many who have to use optical instruments. In numbers they exceed the technical class, and it is obvious that the general education in the subject does not need to go so far for the user as for the designer. Up to a certain point the course for both classes can be identical and I propose to discuss the methods of teaching geometrical optics up to that point and no farther.

In most branches of physical science the technical development of the subject is based upon certain fundamental laws which are incorporated into some sort of mathematical treatment, using the word mathematical in a very broad sense. In nearly all cases it is the teaching of the mathematical treatment that forms the bulk of technical education. The simple laws do not carry one very far technically. It is the practical methods of making use of them and computing their effects that the technical man requires. For example, the general nature of the magnetic field associated with a current flowing in a wire is easily understood by the young student, but he has a long way to go before he can use his knowledge in the design of a three-phase motor.

Now in geometrical optics there is nothing more in the way of physical laws than the two dealing with the reflection and refraction of light and the mathematical treatment involves, at the most, three-dimensional geometry. Except for plane reflections, the whole development of the subject reduces, as far as the technical designer is concerned, to the theory of the symmetrical instrument. Gauss showed that for paraxial rays the relationships between object and image points are contained in the equations

$$Axx' + Bx' + Cx + D = 0 \quad \dots\dots(1),$$

$$y' = y (Ax' + C) = y/(Ax + B) \quad \dots\dots(2)$$

with the relationship  $BC - AD = 1$ .

In these equations  $x, y$  are the co-ordinates of a point in the object space and  $x', y'$  of the corresponding point in the image space. The equations form a geometrical collineation, and transform points into points and straight lines into straight lines. They are not strictly true and are approximately so only as long as the fields and apertures that are dealt with are small. But, all the same, they represent what the designer aims at even for large fields and large apertures and his chief concern in computing a system is to choose the lens curves, separations and glasses so that the image defects are kept within tolerable bounds. The preliminary design of most optical systems is, however, made on the supposition that the Gaussian relationships hold for the full aperture and the full field.

There are, of course, many ways in which these relationships may be written. For example, with a suitable choice of origins the first equation is the same as the familiar  $uv = f^2$ , but no matter what origins of reference be chosen the Gaussian equations form the basis of optical design for all sizes of field and of aperture.

Hence it seems to me that in teaching the subject of geometrical optics more design work on Gaussian lines might be attempted and I should like to see more attention paid to the lateral side of the design and not so much on the longitudinal. I can best illustrate what I mean by a simple example of the type of design work that my own department is continually doing. I need, say, a telescope of the inverting type which has to be used in rather poor light. The telescope is to be used for some purpose of measurement and a knowledge of the sensitivity required suggests that the magnification should be about  $10 \times$  while the light conditions indicate that an exit pupil of not less than 5 mm. should be obtained. We arrive therefore at a 50 mm. objective, and a knowledge of what can be done in the way of correcting the aberrations of the objective and the eyepiece indicates that the objective cannot comfortably be shortened beyond  $f/6$  or in other words that its focal length must be at least 300 mm. This requires that the equivalent focal length of the eyepiece shall be 30 mm. and, knowing that the apparent field cannot be greater than from  $50^\circ$  to  $55^\circ$ , one can decide immediately that the diameter of the field upon the focal plane will be 30 mm. One must then decide what type of eyepiece, Ramsden, Huyghens or Kellner, is going to be used and the Gaussian design of the whole optical system can be completed, drawing it to scale and determining the necessary diameters of the lenses for transmission of the full beam of light.

It is lateral design of this character that forms a useful introduction to the technical end of geometrical optics. I do not assert that this side is never considered at present, but when looking through some of the text books I am constantly struck by the preponderance of examples on the longitudinal side, such as complicated formulae for the apparent distance. I always have the feeling that the authors are using the Gaussian image formation as a convenient peg upon which to hang a lot of complicated algebra. If writers and teachers want to exploit geometrical optics as a subject for the elaboration of mathematical conundrums then, in my opinion, it is better to go further into the only part that gets away from the symmetrical optical instrument, namely the part connected with plane reflections. The geometry here can be quite complicated and to treat it fully a more extensive know-

ledge of spherical trigonometry is required than is usually possessed by the technical optics designer. If the mathematician wants a new scope for his art, that can lead to practical results, I would draw his attention to Mr T. Smith's recent work on *The Theory of Matrices* as applied to the analysis and synthesis of reflecting prism systems.

Far more might be done in the way of instruction in the use of prisms in instruments without any loss to the technical man. Reflecting prisms enter into so many optical instruments and there is any amount of scope for a text book which treats them in a thorough and systematic manner. Such things as the fundamental necessity for an even number of reflections if a right-handed image is required and an odd number for a left-handed image, or the development of prisms into parallel blocks of glass, or the necessity of at least four reflections to cope with the displacement of an object to *any* image position: all these points are of vital interest and are all based upon fundamental conceptions of geometry that ought to be adequately treated. This branch of the subject is full of useful practical examples that can be based upon the more commonly used forms of reflectors, such as the Porro prisms for binoculars, the Prandl prism for rangefinders, the tetragonal or corner-cube prism for returning a beam parallel to itself, and so forth, all of them examples of common practice which every student, whether potential user or potential designer, ought to be thoroughly familiar with.

Again, I wish to urge the desirability of bringing the descriptions of optical instruments more up to date. The telephoto lens in photography, the internal focussing telescopes of theodolites, the rangefinder, the prism binocular, the prismatic astrolabe of the geodetic surveyor, the level, the tachometer, the kinema projector, the process camera, the variable power telescope: here are a number of optical systems in common use embodying a great variety of Gaussian designs that might, with profit to the user and to the designer, be included in a course on geometrical optics. There is scope here for very valuable instruction in the outline design of instruments, particularly of the lateral character that I have previously mentioned. As a side line in instrument design there is the very important question in many visual instruments of the character of the field of view. Many visual instruments require observation to be made by bringing two optical images into contact. The fields may be superposed as in the case of the sextant, or adjacent as in the rangefinder. Optical systems that will give fields of these two types are of importance, and the current practice for the one type or the other might very well be taught. Again, in instruments used for accurate measurement it is very frequently the case that one wants means of measuring small angles by movement of optical parts with open scales. The various methods of achieving this end, the travelling wedge, the sliding positive and negative lenses, the parallel plate micrometer, the Zeiss rotating wedges, are all subjects that give an opportunity for theoretical treatment that is of great practical value.

I have said enough, I think, to indicate my opinion that the teaching of geometrical optics might be brought much more into contact with reality by including a large number of modern instruments and the gadgets that are associated with



them. I am confident that if this is done the course could be made more interesting to the mere user and the technical man could get earlier into touch with the practical side of his subject. It is possible the inclusion of even a part of what I consider desirable may necessitate the excision of something that is already taught. If so, then I should, without question, omit entirely any attempt to teach aberrations except qualitatively. The instruction must be given in such a way that the student does not lose interest. No doubt every lecturer on the subject has his own ideas, but I think it can do no harm if I put down here the methods that I have used and found to be satisfactory.

Quite early in the course, in the investigation of the Gaussian equations for image formation, the student appreciates the fact that in each successive space between refracting surfaces there is, somewhere or other, a field plane  $FF'$  and an aperture plane  $AA'$  (Fig. 1), and that in the symmetrical optical instrument one is interested only in a circular part of the field plane and a circular part of the aperture plane, both circles being concentric with the optical axis. Gaussian formulae are only approximately true; they require that the radii both of the field and the aperture should be small. If we take any ray entering the instrument, it can be shown that in the space we are dealing with the ray should travel from  $P$  in the aperture plane to  $Q$  in the image plane, crossing these planes at heights  $x$  and  $y$  from the axis.

Since the Gaussian equations are not exactly true, the ray will depart from its ideal position  $PQ$  to  $P'Q'$ . It has a lateral aberration  $QQ'$  on the image plane. It is clear that  $QQ'$  must be a function of both  $x$  and  $y$ . It is clear also that by rotating the instrument through  $180^\circ$  round its axis that  $QQ'$  must change sign without alteration of magnitude when the signs of  $x$  and  $y$  are changed without alteration of magnitude; in other words, that  $QQ'$  is an odd-valued function of  $x$  and  $y$  mathematically small in comparison with  $x$  and  $y$ . We can therefore put down immediately

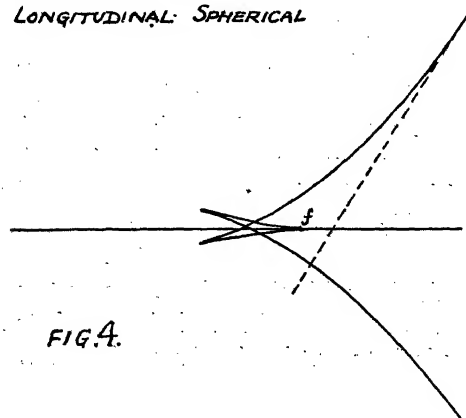
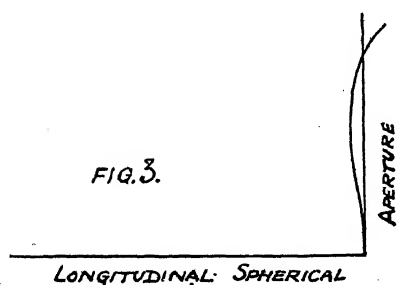
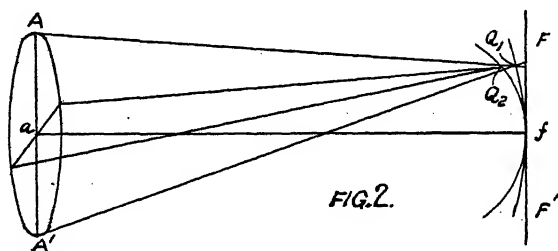
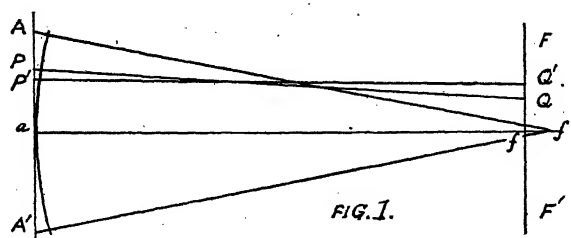
$$QQ' = Ax^3 + Bx^2y + Cxy^2 + Dy^3 + \text{fifth and higher powers.}$$

Omitting for the moment the fifth powers and dealing with what are called first order aberrations, one gets four terms  $Ax^3$ ,  $Bx^2y$ ,  $Cxy^2$ ,  $Dy^3$  which can be utilised to illustrate the nature of aberrations. If the higher order aberrations can be neglected then in the final image space the object of the designer is to make the coefficients zero.

If we take the first term,  $Ax^3$ , alone we can see the effect on the formation at the middle of the field. Take two rays, one through the top and the other through the bottom of the stop. They intersect on the axis, but at  $f'$ , whereas a similar pair of paraxial rays intersect at  $f$ . Calculations of the position of  $f'$  lead easily to the determination of the simple caustic and the nature of spherical aberration becomes apparent. I find it convenient at this stage to call attention to the shape of the wave-front as it emerges from the stop. In the absence of spherical aberration the shape is that of a sphere. With spherical aberration as shown in Fig. 1 the surface has the same radius of curvature on the axis but flattens out as one leaves the axis.

After spherical aberration it is, I think, more convenient to pass directly to the

astigmatism term,  $Cxy^2$ . The trigonometry shows that if the two rays through the top and bottom of the stop be drawn (omitting all the other three terms in the aberration) they intersect at a point  $Q_1$  (Fig. 2) and that as  $Q$  is moved up and down



the field the focussing point traces out a curve of radius  $1/C \cdot af$  and we get immediately the notion of curvature of field. The next point is more difficult and requires a three-dimensional consideration. The wave-front emerging from the aperture

when the image point is on the axis is symmetrical with respect to the axis, although it is not spherical. The wave-front converging to a point off the axis cannot be assumed to be symmetrical with respect to its principal ray but the symmetry of the instrument shows that the principal planes of the wave-front lie, one in the plane of the paper and the other at right angles to it. If, therefore, we were to draw two other rays through the sides of the aperture, they will also intersect one another but at a point  $Q_2$ . The student has, or ought to have, sufficient knowledge of solid geometry to understand what is meant by the two principal radii of curvature and by focal lines, and the extension of these ideas to the second field curvature is not difficult. I am afraid, however, that I have never succeeded in finding an easy method of showing that the curvatures of  $fQ_1$  and  $fQ_2$  are invariably of the form  $3X + Y$  and  $X + Y$ , where  $X$  represents the astigmatism and  $Y$  the Petzval curvature. Usually I have stated plainly that these facts emerged clearly from a quantitative examination of the aberrations and could not be easily demonstrated in a simple manner.

I have said enough, I think, to indicate that, as far as spherical aberration and astigmatism are concerned, they can be explained to elementary students in a qualitative manner. Coma and distortion follow in the same way and the student can thus be familiarised with the five von Seidel aberrations so as to be able to understand the problems that face the optical designer in his attempts to produce satisfactory optical instruments. One cannot go much farther. Practical design involves consideration of higher order aberrations, generally by some system of trigonometrical ray tracing. It involves not the removal of the first order terms but a balancing of their residual values against those of higher orders. But I used to find that in respect of spherical aberration it was worth while carrying the matter a stage farther. The customary method of plotting spherical aberration as derived from ray tracing is shown in Fig. 3. As the aperture is increased in a well-corrected system it is common to find that the under correction of spherical aberration increases up to a maximum and then diminishes. For the extreme rays it is frequently over corrected. Let the student plot even roughly the caustic that corresponds to a spherical aberration distribution of this sort and he has no difficulty in arriving at the three-cusped curve shown in Fig. 4. The emerging wave-front has minimum curvature on the axis and maximum curvature at a zone off the axis. This side-light on image formation is of considerable practical interest because the student is able to appreciate that the circle of least confusion is by no means at the position assigned to it when aberrations of the first order only are dealt with.

One cannot go much farther with aberrations. Any attempt to establish their quantitative values by the use of some form of characteristic function should be kept entirely for the technical student in his advanced course.

## GENERAL DISCUSSION

Mr T. B. VINYCOMB: I should like to emphasise Dr Searle's remark that the pupil should have precedence in the choice of the method of presentation of a subject. Last summer I marked 250 scripts written at the Intermediate and Higher Schools Examination. In the paper was a simple question on a lens. 247 candidates attempted it and 7 solved it. All the 240 who failed in their attempts used the formula  $1/u - 1/v = 1/f$ . All four who used  $1/u + 1/v = 1/f$  solved the question. As the candidates came from all parts and had different teachers it is clear that the convention of signs used in the first formula is not grasped by pupils at this stage. Those who are going further in their studies can be expected to be able to deal with any reasonable convention of signs, but elementary students should not have their difficulties increased unnecessarily.

Mr W. BENNETT: It is probable that few teachers of experience have not at some time experimented in the introduction of beginners to the subject through the method of curvature. It is also probable that very few have retained it as their principal method of approach. The reasons for retaining the ray method have been well put by several speakers, but I should like to point out another advantage. In approaching the simple lens by the ray method we have to indicate, by the approximations that we make, within what narrow limits the simple lens can be expected to form good images, and the pupil is in a position to appreciate the wonder of modern instruments. If we approach by way of the wave-front we can assume at this stage only that the emergent wave-front is spherical, and we have no indication of the degree of exactness of this assumption. Light tracks may be used without any special apparatus. A modern gas-filled lamp, placed with its axis horizontal some way behind a slit fixed to the edge of a drawing board gives a track with which much very useful work may be done. I should like to plead strongly for the retention of the formula  $1/u + 1/v = 1/f$ . It is much the simplest form to use with the optical bench, and indeed, as has been pointed out, any other form leads with elementary students to endless confusion. The objection is raised that with this convention the formula becomes inconvenient when a ray has to be traced through several lenses or surfaces, but surely the formula is the very worst to use for such a purpose, and in serious computation it is not used at all.

Mr A. G. TARRANT: As I have tried out a number of different methods of approach to this subject during the last nine years, my personal experience may be of interest, since, after all, the proof of the pudding is the eating. At first I tried beginning with the physical nature of light. But later experience has shown me the wisdom of being much less ambitious, and now I begin with the observed facts of light propagation, reflection, and refraction. This has the advantage of giving the students, from the first, ideas that are clear-cut and certain. Experience has shown that my students, at any rate, follow this order very much better. To begin in this

way with incontrovertible results of experiment has the added advantage of emphasising a very important point. For it is the function of theory to explain the results of experiment, and the function of experiment is to find out what are the facts concerning any phenomena, not to illustrate theory. In every science accurate knowledge of fact must precede theory. In these days of rapid advance in theory we are in danger, sometimes, of forgetting this, and we ought to be specially careful in training the rising generation of physicists to keep observation and theory in their proper order and relation.

It would seem particularly desirable in this subject to preserve this order, as if we begin with the physical nature of light we are at once faced with our own ignorance. What is the physical nature of light? Which theory, Fresnel's, Maxwell's, Planck's, Schrödinger's, shall we teach? Matters that are still the subject of theoretical argument would seem best avoided with beginners, and for that reason, if for no other, it has seemed best to me, after mature consideration, to keep to the old-fashioned, but clear, safe and certain method of taking the observed facts first.

#### COMMUNICATED REMARKS

Dr TERRY THOMAS: My impression is that it is much more difficult for young boys to grasp the implications of the wave theory. They are much happier with lines and points, and, of course, their geometry can be made useful in this connection. Nevertheless I feel that the teaching on optical instruments is generally not satisfactory and I think the text-books are very largely to blame. I very much doubt if many boys leaving school, or even university, students have a very clear idea of optical instruments. Probably not enough attention is given to the fitting up of such instruments in the laboratories. Too often, if they are used at all, they are used in the complete manufactured state.

Mr F. RECORD: In the Technical College, Derby, we have used the wave method for teaching the properties of mirrors and lenses for some years and are satisfied that it provides a more complete physical account of the action of such appliances than does the ray method. As the result of our experience, we suggest that the diopetre be defined as a unit of curvature. After having shown that the curvature of a wave-front or surface is measured by the reciprocal of the radius, we seek for a unit of curvature. If we choose for the unit the curvature of a surface whose radius is one metre and call it one diopetre, we find naturally that we have a unit for measuring the power of a lens or mirror. This is so because the power is the curvature impressed by the appliance on the incident wave-front. I would like to say how useful the graphical method described by J. H. Dowell\* has proved in teaching the principles of the direct vision spectroscope. With a little care in drawing the surfaces in the sketch of the prism and in the scale diagram in the same direction, the whole of the facts with respect to the direct vision prism are presented in a manner which appeals to students. There seems to be no other method which gives so much information in so compact a form.

\* *Proc. Optical Convention*, 2, 965 (1926).

Mr A. W. BARTON: There is one small point which I should like to raise although it is rather off the trend of the main line of the discussion. The subject of photometry has rather gone to seed in recent years as far as school work is concerned, but within the last ten years a very striking application of the law of inverse squares as used in photometry has been made. I refer to the determination of the distance of star clusters and spiral nebulae by the measurement of the apparent brightness of Cepheid variables contained therein. The periodic time of the variable star fixes its illuminating power (i.e. candle power) and so its distance can be calculated. It is in this way that Hubble has estimated the distance of the remotest spiral nebulae at 140 million light years. I feel that such a wonderful application of the fundamental principles of photometry would do much to put fresh life into the subject and should certainly be included in any elementary treatment of the subject.

Prof. L. C. MARTIN: Why teach geometrical optics at all? There are two main justifications for the teaching of any subject: firstly, its possible educational value; secondly, the utility of the knowledge acquired.

I shall venture to express no opinion on the educational value of geometrical optics considered merely as a branch of higher applied mathematics, but it is generally conceded that the utility of much that has been taught in this connection is extremely meagre. It seems to be the case at present that the mathematical purist is somewhat out of his depth when the more complex practical problems of applied optics are encountered, problems which yield only to numerical methods of the "try, try, again" type, as intelligently conducted as possible. This is not said in order to detract from, but rather to emphasise the necessity of, further mathematical research by those qualified to undertake it. The ordinary science student encounters geometrical optics as a branch of physics; he does not reach the stage of mathematical refinement, but has to be content with elementary principles. It is usually understood that the object of the instruction is the attainment of some knowledge of the principles of the optical instruments which he is bound to employ in observation and measurement.

It is unfortunately the case that the Gaussian lens theory to which the elementary student is early introduced rests on a basis of approximation which is not exactly understood, in the usual way, either by the teachers or the taught. The simple trigonometrical tracing of a few rays through a lens might let in a flood of light on the whole subject. I would never introduce a student to the theory of a lens till he has understood the trigonometrical method of exact ray tracing, till he has explored the conditions of refraction at a single spherical surface, and grasped the idea of the curvatures of corresponding object and image fields in that simple case.

The idea of aberration, a terrifying subject to many, can be introduced in one of the earliest pin-method experiments in ray tracing through a plane surface. Then ray tracing, by the aid of Snell's construction, on the drawing board will give a sense of power and exactness which are entirely lacking in the ordinary approach to lens theory.

Then again, a close connection between physical and geometrical theory needs to be maintained throughout the instruction. The idea of the "optical path"; the elementary image as the meeting point of disturbances arriving in the same phase; the aspect of aberration as optical path difference; all these can be introduced in early stages so that the subject develops in a natural and harmonious manner. The Gaussian theory rests very naturally on a basis such as is developed above, and its limitations can be kept clearly in view; the Abbe equations for magnification and for conjugate distances reckoned from the focal points ought to be among the earliest taught instead of being almost entirely disregarded.

Many of these ideas have been worked out in the courses which are being given in the Technical Optics Department of the Imperial College. Prof. Conrady's work is of such a nature that it must in due time have a far-reaching influence on the subject. His methods are set forth in part in his recent book on *Optical Designing and Computing*, Part I. The present writer is also engaged in the preparation of a manuscript on applied optics in which some of the ideas expressed above are worked out on elementary lines in close harmony with Prof. Conrady's methods, the notation and sign conventions therein adopted being mainly used.

Through the courtesy of Mr Emsley, a general agreement as regards notation has been reached between the Imperial College and the Optical Department of the Northampton Polytechnic. A notation for general use, however, must not conflict with that adopted for the theory of ophthalmic lenses in which the use of capitals is generally to indicate the reciprocal of the length denoted by the corresponding small letter. As I strongly deprecate the use (for ordinary students' work) of complicated notations involving types of different thickness, etc. which may cause confusion, it has been agreed to use capital letters of the cursive form to denote the reciprocals of length, thus

$$\mathcal{L} = 1/l,$$

while  $L$  in ordinary type can still stand for a marginal distance in the notation of the computer. The great desirability for a notation is easy writing, a matter seemingly overlooked by many who are fond of introducing complicated types.

Optics has the reputation of being a dry and forbidding subject; in recent years the unnatural separation of the Physical and Optical Societies has not encouraged interest in optics amongst teachers of physics. It is more than time that this separation should be ended by union into two groups of one society with joint meetings of both groups frequently arranged, and the option for members of subscribing to one or both sets of transactions.

SUMMARY OF AGREED NOTATION FOR USE IN ELEMENTARY CLASSES OF THE TECHNICAL OPTICS DEPARTMENTS AT THE IMPERIAL COLLEGE AND NORTHAMPTON POLYTECHNIC

*Designation of Points.*

Object and image	$B, B'$	Nodal points	$N, N'$
Focal points	$F, F'$	Surface vertices	$A_1, A_2$ , etc.
Principal points	$P, P'$		

*Distances.*

	Paraxial	"Marginal" values (computing notation)
Object and image from $P$ and $P'$	... $l, l'$	$L, L'$
Size of object and image	... $h, h'$	$H, H'$
Incident height on surface	... $y$	$Y$
Distance from $F$ and $F'$ to object and image	$x, x'$	$X_f, X_{f'}$
Separation of systems	... $d_1, d_2$ , etc.	
Separation of adjacent focal points	... $g$	
Focal lengths, i.e. $PF, P'F'$ (opposite in sign numerically)	$f, f'$	
"Vertex focal lengths"	... $f_v, f'_v$	
Distance to tangential and sagittal foci	$s, t$ and $s', t'$	
Radii of pupils	... $p, p'$	
Radius of curvature	... $r$	

*Angles.*

Incidence and refraction	... $i, i'$	$I, I'$
Ray with axis	... $\alpha, \alpha'$	$U, U'^*$
Refractive indices	... $n, n'$	$N, N'^*$
Magnification = $h'/h$	... $m'$	$M'$

*Reciprocals.* Focal powers, curvature, and reciprocals of distances to be expressed in capital letters of the cursive form, thus:

$r$ = radius of curvature.	$\mathcal{R}$ = curvature (dioptries) = $1/r$ .
$f'$ = focal length.	$\mathcal{X}$ = focal power = $1/f'$ .
$l$ = object distance.	$\mathcal{L}$ = vergence to object = $1/l$ .

This notation is not used in the computing classes where  $1/r = c$ , but although the employment of capitals to denote reciprocals is securely founded in the theory of ophthalmic lenses, it is suggested that the consistent use of the cursive form will save confusion with an equally well established computing practice of using the Roman capital to distinguish a "marginal" distance.

*Sign conventions.* These are expressed diagrammatically in the accompanying figure.

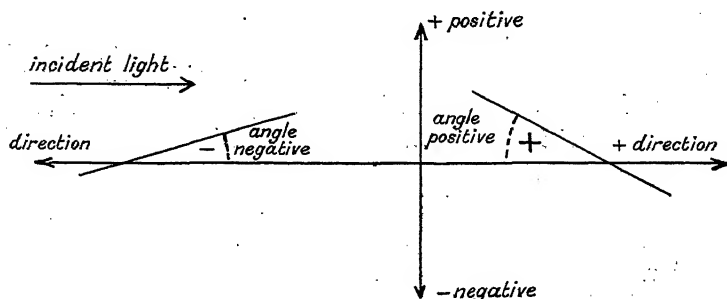
*Surfaces and elements.* Surfaces are numbered consecutively 1, 2, 3, etc.; lenses are given letters  $a, b, c$ , etc.

\* Note that in the computing formulae, the paraxial and marginal angles are  $u, U$ . The use of  $u$  is to be avoided, however, for elementary students who have been used to the Coddington notation of  $u$  and  $v$  for object and image distances. Also  $N$  is to be used for refractive index in computing classes, and  $n$  in elementary classes



*Reduced distances.* Denoted by adding a bar over the corresponding letter, thus  $\bar{l} = l/n$ .

It will thus be seen that the notation adopted in the various technical classes will in future have a great measure of consistency; the great aim is to adopt a notation and especially a consistent sign convention so that elementary students may be saved confusion on proceeding to more advanced work and reading.



MR WILLIAM R. BOWER: A hasty glance through the advanced proofs shows firstly a very notable conflict of opinion, and therefore the urgency of a standardisation of methods, nomenclature, notation, etc. Secondly, that the subject has been handled too much by the non-experimental mathematician, and too little by the physicist, and is therefore terribly susceptible to the hectic influence of examinations. It is certainly time that representative physicists should do something for the betterment of optical education. And may I say incidentally, that not only is optics in distress educationally, but other major branches, especially mechanics, have been over-dosed by mathematicians and the indigestion too easily tolerated by the engineering and experimental physicists. In regard to the teaching of elementary optics, the advanced proofs show that there is, in the main, a conflict between the ray method, with formulated reciprocals, and the wave or curvature method. In my experience the ray method has been the better one. But the wave method when used sparingly is interesting and instructive. The ray method is more easily tackled and when rays have been drawn graphically the wave-fronts are easily traced as arcs perpendicular to the rays. To me the Gauss generalisation of principal points and foci, and the centres (nodal points) of Thomas Young form the basis of geometrical optics. By using several of the fundamental properties of double-ratios, properties that can be easily understood and applied by young students of average mathematical ability, the Gauss and Young points can be easily obtained by simple Geometry, and for direct and oblique incidence. The thick lens would be treated first. The reduction to thin lenses requires a little infinitesimal geometry, like the orthodox analytical method. Prisms, usually neglected, can also be dealt with. The theory should be accompanied by a well-systematised laboratory course to test the results experimentally, and a well-organised exercise class, that would include especially drawing with instruments on an adequate scale the more important loci of object and image. This can be easily and accurately done and proves of great interest as a survey and exploration of the optical field. Such drawings to

a pupil with a "geometric eye" have as much force and flexibility when effectively practised as models and experiments, indeed they are experiments in descriptive geometry. Optical instruments, spherical and chromatic aberrations, and the composition of individual sets of cardinal points into a resultant set for the whole system may also be displayed. The translation of the geometrical results into algebraic formulae either of the Newtonian or reciprocal type may be done at the end of the exercise. Thomas Young, in one of his writings—I regret that at the moment I cannot give the reference—stated very emphatically that for real enlightenment purely geometrical procedures were superior to analytical. This may have been associated with his paper on a centre for oblique refraction at a spherical surface, a centre that was adopted later by Cornu and Weierstrass. May I refer to papers by me in the Society's *Proceedings*\*, in which some of these matters are crudely discussed.

Reply by Mr T. SMITH: It is obviously unnecessary for me to attempt a general summing up of the evidence that has been brought forward in the course of this discussion, but I would like to refer to two or three points of importance that have arisen. We all know that no teacher can afford to disregard the examination syllabus and neglect the kind of question that is set, but in spite of the temporary difficulty thus caused I believe that many teachers will sympathise strongly with Mr Vernon's emphasis on the cultural value of the instruction to be given. In this respect the geometrical treatment, in my judgment, inevitably fails, though, as indicated by Mr Vernon and Mr Emsley, it can be employed effectively in revising work originally treated on the wave basis. Mr Vernon's difficulty about sign conventions can be overcome by interchanging the object and image spaces. Mr Tarrant's objection about waves or quanta involves no difficulty, for we are always dealing with statistical resultants, and the simple wave theory is sufficient.

It would be easy to read into Mr Vinycomb's interesting figures more than they are entitled to convey. My experience in examining scholarship papers taught me that, with the exception of a rare student of outstanding ability, the quality of the teaching, rather than the knowledge and skill of the pupil, is being scrutinised. I would add, while mentioning examinations, that questions in terms of wave concepts, involving numerical answers that can be marked rapidly, may be set as readily as those now common: indeed most questions of practical interest can be dealt with more concisely by the wave treatment.

It has been suggested that the geometrical method has a decided advantage over the wave treatment in exhibiting the degree of approximation reached. The exact contrary is the fact. Moreover, it should be remembered that the physically significant quantity is the difference of path: other geometrical magnitudes may prove most misleading. As an extreme example an infinitely great longitudinal focal displacement (almost the only quantity considered in geometrical discussions) may correspond to a vanishingly small, and therefore physically imperceptible, difference of path.

\* *Proc. Phys. Soc.* 25, 160 (1913); 26, 212 (1914).

Two points emerge unmistakably from this discussion. First, difficulties are experienced in the traditional presentation of the theory, and many teachers have given much thought to the way in which they can best be met. Secondly, judging from a scrutiny of the contributed papers, there is a decided majority in favour of adopting one particular course on some of the more debatable questions, such as the sign conventions. Since the existing divergencies cause considerable trouble to students, an attempt might well be made to see whether general agreement on these points can be reached, and I should like this meeting to express its views on the suggestion contained in Mr Williams' paper that the Council of the Physical Society should approach the Science Masters' Association and other interested bodies with a view to the appointment of a joint committee to make recommendations on these matters.

## GENERAL SURVEY OF THE EFFECTS OF PRESSURE ON THE PROPERTIES OF MATTER

BY PROF. P. W. BRIDGMAN, Hollis Professor of Mathematics and  
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*The Fourteenth Guthrie Lecture, delivered April 26, 1929*

PROF. RICHARDSON has intimated that an acceptable subject for this lecture would be a general survey of my experiments on the properties of matter under high pressure, and I have accordingly made this choice. I feel, however, that this choice demands some apology on two counts: first, because little of what I have to say is new; and second, because the subject, concerned as it is with the properties of matter in bulk, is not to-day one of the most lively interest. There are, nevertheless, certain points of view from which such a topic may be regarded, on the contrary, as especially timely. If the Bohr-Heisenberg principle, with the radical change in our physical point of view which it involves, turns out to be correct, it will not be possible to make indefinite further progress in the direction of the analysis of the very small, and physics must soon return to the task of explaining the properties of matter in bulk, a task which has been temporarily laid aside. Furthermore, the Bohr-Heisenberg principle suggests that matter in bulk may have properties not deducible from the measurable properties of its smallest parts; if this is the case, it becomes doubly important to investigate the large scale properties of matter under those especially simple changes of condition produced by hydrostatic pressure. But in order that hydrostatic pressure may produce significant changes, it is necessary that it be of the same order of intensity as the atomic or molecular forces themselves, and these, for ordinary solids or liquids, are of the order of tens of thousands of kilograms per square centimetre. The point of the experiments upon which I am to report is that the pressures are of this order of magnitude.

This is not the place to go into questions of technique. It will be enough to say that by the use of a packing of special design, which automatically becomes tighter at higher pressures, the problem of leak disappears, so that the only limit to the pressure attainable is set by the cohesive strength of the walls of the containing vessels.\* By the use of alloy steels, and of vessels of small size, so that the beneficial effects of heat treatment may be extended throughout the entire wall, pressures up to more than 20,000 kg./cm.<sup>2</sup> can be handled and measured with an accuracy of 0.1 per cent. Most of my experiments, however, are made to only

\* The way in which the automatic tightening of the packing is produced in the case of the plunger by which pressure is generated is shown in Fig. 1. This represents a section of a cylinder

12,000 kg., in the interests of economical life of the apparatus. There was, of course, a great deal of preliminary development work to be done in finding the best designs of the containing vessels, in developing methods of measuring pressure, and in devising means of measuring various properties of small amounts of substances enclosed in heavy steel vessels, but I leave this aspect of the subject to discuss the effects of pressure on various properties of matter.

Perhaps the most significant and certainly the simplest of the effects of pressure is diminution of volume. The change of volume of any truly homogeneous substance, free from internal strains, is entirely reversible with pressure; no permanent change of volume has ever been observed in such materials up to pressures at least as high as 25,000 kg. Contrary statements sometimes found in the literature are to be explained either by flaws in the material or else by failure of the pressure to be truly hydrostatic, as when pressure is transmitted by an oil which freezes under pressure, thus producing permanent changes of figure in the material.

in which pressure is generated in a liquid, *L*, by the advance of a piston of hardened steel, *P*, driven by a hydraulic press. The mushroom-shaped plug, *A*, carries a collar, *C*, of soft rubber packing. The plug with the packing is pushed forward by the piston *P* acting on the intermediary ring of hardened steel *D*. The space, *E*, at the end of the stem of the mushroom is empty, so that the

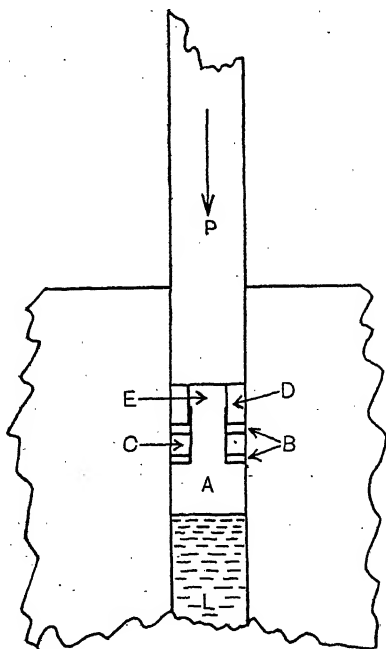


Fig. 1.

total pressure exerted by the ring of rubber must equal the total pressure exerted by the liquid on the head of *A*, and since the area of the ring is less than the area of the head, the pressure in lb./in.<sup>2</sup> in the rubber is always greater than that in the liquid by the ratio of the areas, and the liquid can never leak. The packing is prevented from escaping by rings, *B*, of mild steel or copper. Further details of the technique are described in *Proc. Amer. Acad. Arts and Sci.*, 49, 627-643 (1914).

The compressibility of fluids is, of course, in general much greater than that of solids. There is no essential distinction in compressibility between a substance ordinarily liquid and one of the so-called permanent gases, beyond the initial few thousand kilograms of pressure, which is far higher than the critical pressures between liquid and gas. It was shown by Amagat that air, for example, at a pressure of 3000 kg. is as dense as water.

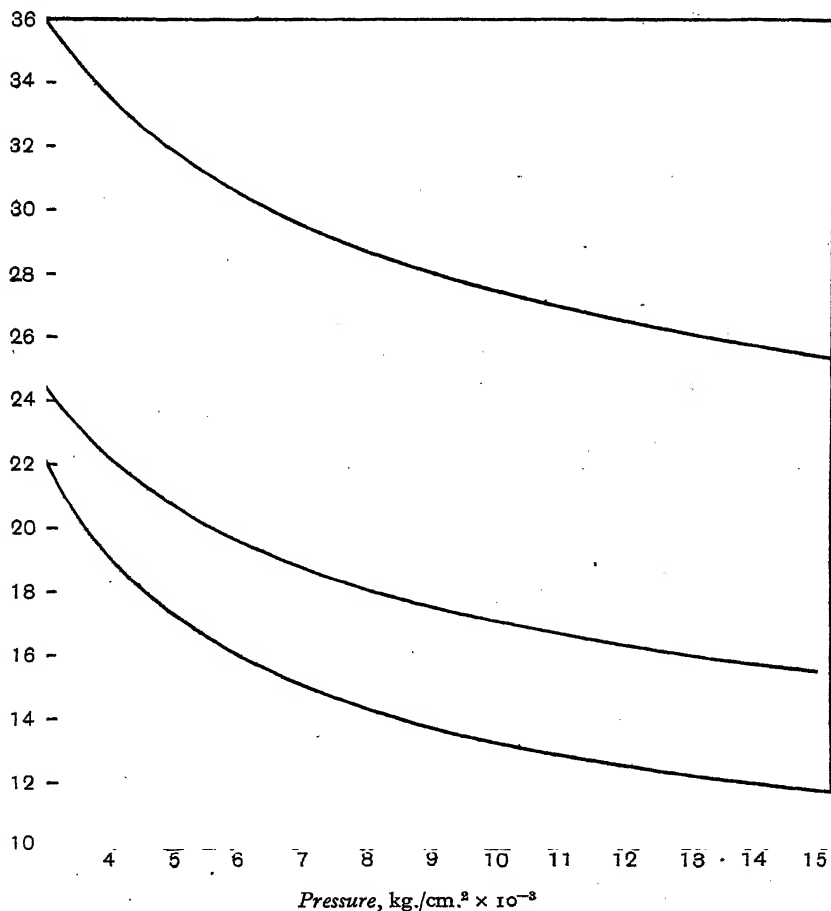


Fig. 2. The volume in c.c. per mol. as a function of pressure at 65° of nitrogen, hydrogen, and helium, reading from the top down.

The chief experimental difficulty in measuring the volume of gases at high pressures is the enormous initial volume, which makes it necessary to introduce the gas into the high pressure apparatus in small bombs in which it is subject to a high preliminary compression. In Fig. 2 is shown the volume in cm.<sup>3</sup> per gm. molecule of N<sub>2</sub>, H<sub>2</sub>, and He between 3000 and 15,000 kg./cm.<sup>2</sup>. The order of volumes is what is to be expected, monatomic He having a smaller volume at all pressures than biatomic H<sub>2</sub>, which in turn has a smaller volume than N<sub>2</sub>, also biatomic, but with

a much more complicated molecule. In Fig. 3 the product  $p\bar{v}$  of these three gases is plotted after the manner of Amagat as a function of pressure. Departures of  $p\bar{v}$  from unity are a rough measure of the departure of the behaviour of the substance

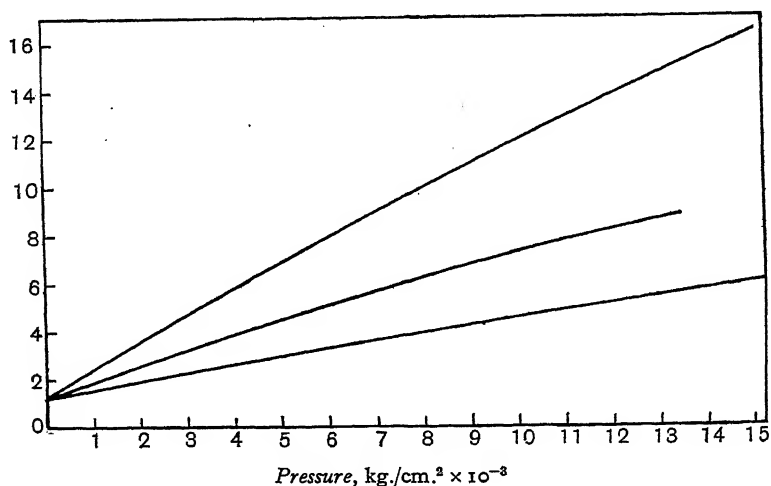


Fig. 3. The product  $p\bar{v}$  as a function of pressure for nitrogen, hydrogen and helium (curves reading from the top down).  $p$  is the pressure in  $\text{kg./cm.}^2$  and  $\bar{v}$  is the volume of that amount of gas which under a pressure of  $1 \text{ kg./cm.}^2$  occupies  $1 \text{ c.c.}$  at  $0^\circ \text{C.}$

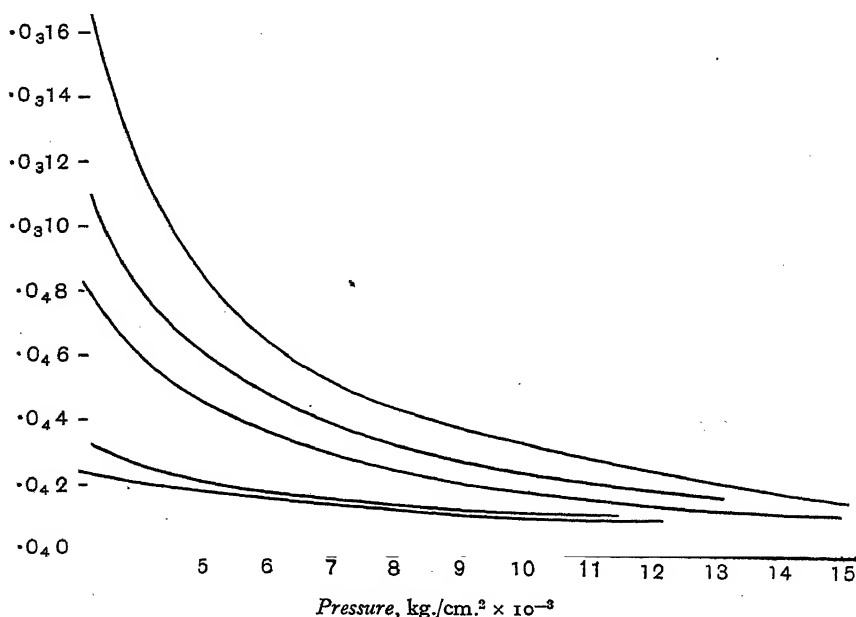


Fig. 4. The instantaneous compressibility,  $\frac{1}{\bar{v}} \left( \frac{\partial \bar{v}}{\partial p} \right)_\tau$ , as a function of pressure, of helium at  $55^\circ$ , hydrogen at  $65^\circ$ , nitrogen at  $68^\circ$ ,  $\text{CS}_2$  at  $65^\circ$ , and water at  $65^\circ$ , reading from the top down.

from that of a perfect gas. The departures found by Amagat up to 3000 kg. are seen to continue to become greater at very nearly a constant rate up to the highest pressure reached. Again, the behaviour is as is to be expected; He approaches most nearly to the perfect gas condition, although at 15,000 kg. its volume is six times greater than if it had remained a perfect gas.  $N_2$  departs most widely from

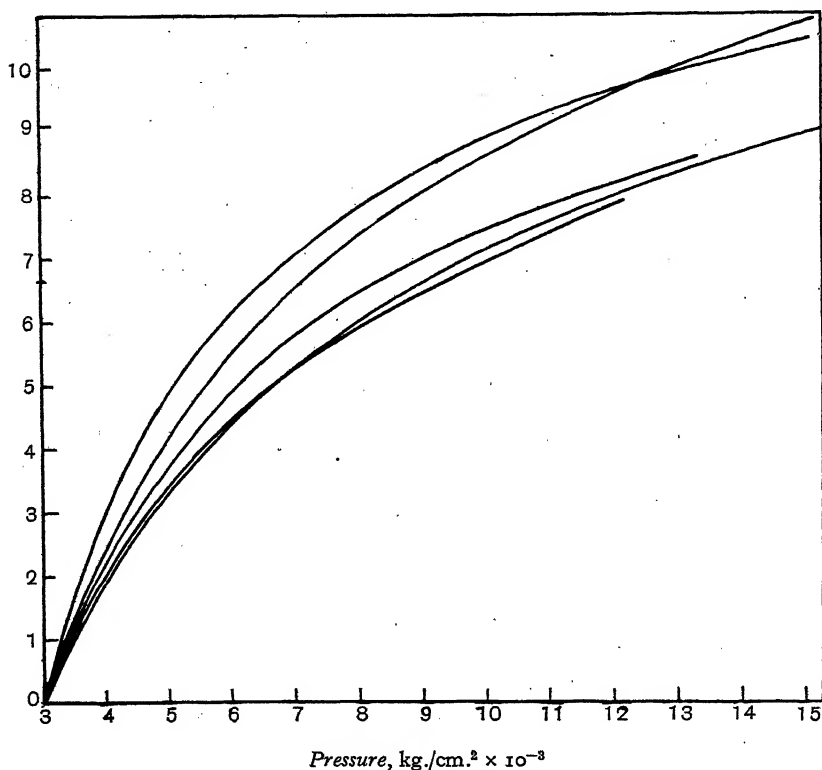


Fig. 5. The change of volume in cc. per mol as a function of pressure, reckoned from 3000 kg./cm.<sup>2</sup> as the fiducial pressure. At 10,000 kg./cm.<sup>2</sup> the order of the curves, reading from the top down, is: helium at 55°, nitrogen at 68°, hydrogen at 65°, argon at 55°, and ammonia at 30°.

the perfect gas, while  $H_2$  is intermediate. In Fig. 4 the "instantaneous" compressibility,  $\frac{1}{v} \left( \frac{\partial v}{\partial p} \right)_T$ , of the three gases is shown and also, for purposes of comparison, the instantaneous compressibility of liquid  $CS_2$  and water. At the lower pressures, in the neighbourhood of 3000 kg., the compressibility of the gases is several fold greater than that of the liquids, but at the highest pressure, 15,000 kg., the compressibility of all is nearly the same.

Thus far the behaviour of gases at high pressures has been a natural enough extension of the behaviour at low pressures. There are, however, effects at high pressure which would not naturally be inferred from the behaviour at low pressures. Fig. 5 shows one such effect, namely, the change of volume in cc. per mol, starting from the volume at 3000 kg. as the fiducial volume, for the five gases  $H_2$ , He,  $NH_3$ ,



$N_2$  and A. The significant feature is the crossing of the curves for  $N_2$  and He; it is evident, furthermore, that the curves for  $H_2$  and A will also cross at a pressure slightly higher than that shown in the figure. The qualitative significance of this is as follows. At comparatively low pressures, the decrease of volume of a gas has its origin in a decrease of the empty space between the atoms or molecules, but as the molecules are pushed into closer contact, this effect becomes exhausted, and at high pressures this contribution to compressibility disappears. But there is another factor in the compression, namely, the actual loss of volume of the molecules themselves, and this evidently may persist at pressures where the initial effect no longer exists. This dual mechanism is doubtless the explanation of the striking difference between He and  $N_2$ . The atom of He is much smaller than the molecule of  $N_2$ , so that at low pressures the decrease of volume of He is greater than that of  $N_2$ . But at high pressures, where the important factor is the loss of volume of the atoms or molecules themselves, the decrease of volume of  $N_2$  becomes greater than that of He, because the structure of the  $N_2$  molecule is so much more complicated than that of the He atom that it has in it the potentiality of much greater loss of volume. The same sort of considerations also explain the relative behaviour of  $H_2$  and A. The molecule of  $H_2$  is normally smaller than the atom of A, so that at low pressures the compressibility of  $H_2$  is greater than that of A. But at high pressures the rôles are reversed, because the electronic structure of atomic A is so much more complicated than the electronic structure of molecular  $H_2$  that the atom of A is capable of much greater loss of volume than the molecule of  $H_2$ .

This behaviour, so definitely shown by these gases, is typical of the behaviour of all substances at high pressures. Beyond the first few thousand kilograms, the major part of the loss of volume is provided by the atoms or molecules themselves, and those substances with the most complicated or the most loosely constructed molecules have the greatest compressibility at high pressures, although at low pressures the behaviour may be the reverse. All this does not mean that a molecule is not properly to be regarded as a field of force rather than as a little nugget of matter in the old-fashioned sense, but it does mean that when the molecules are pushed closer together, there are qualitative changes in the interaction of their force fields similar to those which the older picture suggested.

Passing next to the volume behaviour of liquids, the most immediately striking fact is that the volume changes of many liquids tend to approach much more nearly to equality at high pressures than at low. Measurements on fourteen common liquids, including the first five alcohols, ether,  $CS_2$ ,  $C_2H_5Cl$  and water, show an extreme variation in the loss of volume under 12,000 kg. from 21 per cent. for water, the least compressible, to 33 per cent. for ether, the most compressible, which thus under 12,000 kg. loses only 50 per cent. more volume than water, although its initial compressibility is four or five times greater. The compressibility of liquids drops very rapidly with increasing pressure as is shown in Fig. 6. At 12,000 kg. the compressibility of common organic liquids varies from 1/14th to 1/20th part of the initial compressibility; half of the drop to the final value is accomplished in the first thousand kilograms, and at 6000 kg. the drop is 95 per cent. completed.

Qualitatively, there is thus much similarity between liquids and gases. As in the case of gases, the initial high compressibility of liquids arises from the taking out of slack between the molecules, whereas the part of the compressibility which

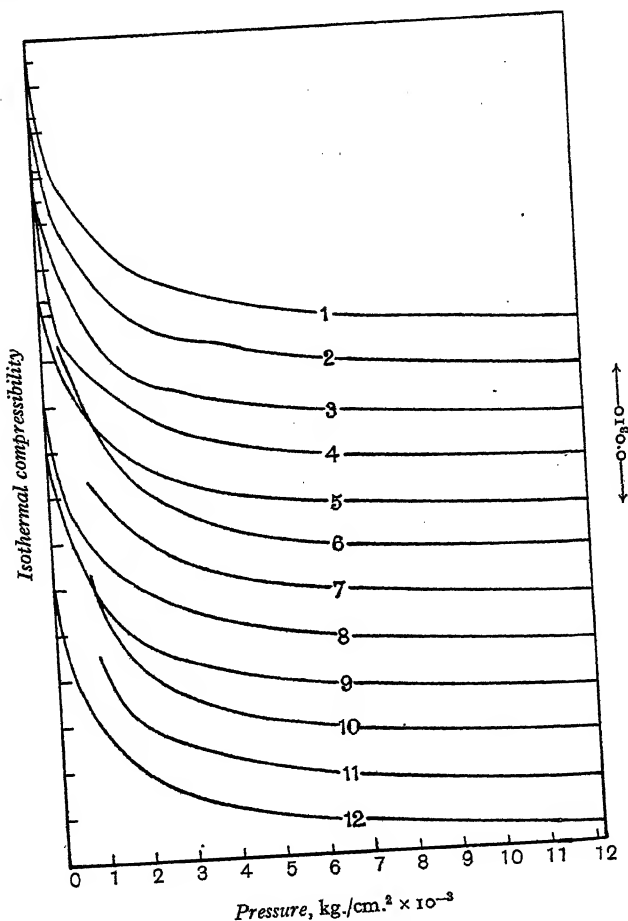


Fig. 6. The average compressibility between 20° and 80° of twelve liquids as a function of pressure. In order to prevent overlapping, the origin of each curve has been displaced one square with respect to the next. The scale of the curves is shown on the right hand side. The origin is so situated that the compressibility of each of the twelve liquids at 12,000 kg./cm.² is between 0.001 and 0. The numbers on the curves indicate the liquids as follows: 1, methyl alcohol; 2, ethyl alcohol; 3, propyl alcohol; 4, isobutyl alcohol; 5, amyl alcohol; 6, ether; 7, acetone; 8, CS<sub>2</sub>; 9, PCl<sub>3</sub>; 10, ethyl chloride; 11, ethyl bromide; and 12, ethyl iodide.

persists to high pressures probably arises from the decrease of volume of the molecules themselves. Liquid metals, as is to be expected, have a lower order of compressibility than organic liquids; it is also surprising that glycerine, which has a fairly complicated molecule, is only two-thirds as compressible as water at 12,000 kg.

By measuring the volume as a function of pressure at different temperatures it is possible to find how thermal expansion varies with pressure. The results for twelve different liquids are shown in Fig. 7. As was to be expected, thermal expansion drops with increasing pressure, but it is perhaps surprising that the decrease is much less than the decrease of compressibility; the thermal expansion under 12,000 kg. is on the average between one-fourth and one-fifth of its initial value, against four times as great a decrease in compressibility. Furthermore, the thermal

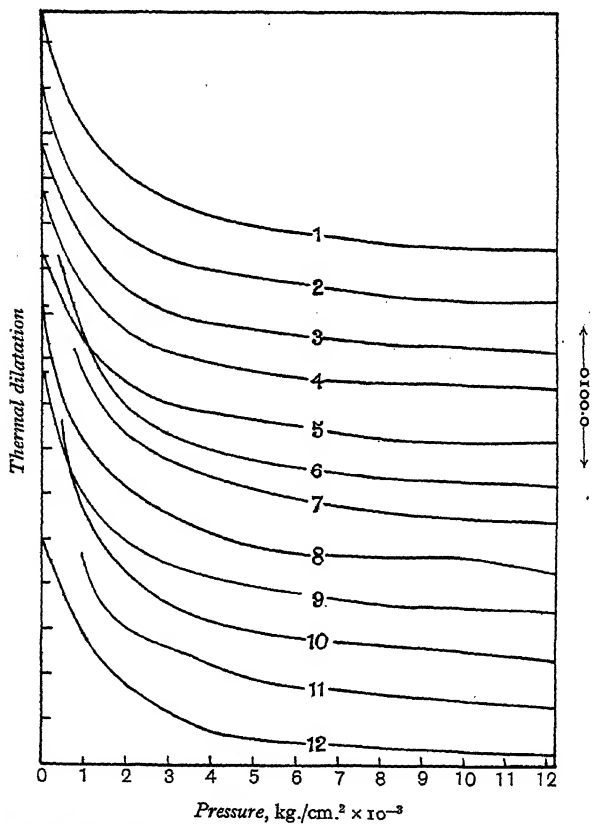


Fig. 7. The average thermal expansion between 20° and 80° of twelve liquids as a function of pressure. The general method of representation is the same as in Fig. 6, except that the origin for each curve is so situated that the expansion at 12,000 kg./cm.<sup>2</sup> is between 0.0002 and 0.0003.

expansions of fourteen liquids, with the exception of water, approach much more closely to equality under 12,000 kg. than do the compressibilities, the extreme variation being by only 25 per cent., from  $2.4$  to  $3.0 \times 10^{-4}$ .

It is natural to expect parallelism between the effects of high pressure and low temperature, since both have a tendency to constrain freedom of internal motion, but the parallelism is far from complete, because as temperature approaches 0° abs., the compressibility drops only slightly, while the thermal expansion drops

to zero, but at high pressures the compressibility drops much more than the thermal expansion.

At atmospheric pressure the thermal expansion of all liquids increases with increasing temperature, but in the neighbourhood of 3000 kg. there is a reversal, and at higher pressures thermal expansion is greater at lower temperatures than at higher. The explanation is probably connected with the known fact that if the molecular restoring forces in a solid are linear functions of the molecular displacement, thermal expansion vanishes, so that a high thermal expansion means high departure from linearity. The smaller the volume of a substance the greater in general the departure of the forces from linearity, since the repulsive forces which predominate at small volumes vary inversely as some high power of the distance. At constant pressure the volume is less at low temperature, so that the departure from linearity would be expected to be greater, thus accounting for the greater thermal expansion. At low pressures there is a reversal of this behaviour because there is another mechanism active, the liquid tending to approach more nearly to a gas, with its high thermal expansion, the higher the temperature.

Superposed on the broad features just described, common to the behaviour of many liquids, there are small-scale specific differences of an almost indescribable complexity. An inspection of the experimental data would make it evident that an enormous number of parameters would be necessary to describe in full detail the behaviour of even a single liquid, and the small-scale complexities of different liquids are without discoverable relation to each other. This means that no such thing as a general equation of state for liquids can exist, and that the most that can be expected is to find an equation which shall reproduce the broad common features of behaviour described above. Very few attempts have been made in this direction, and as far as I know, none have been successful.

The volume behaviour of solids is qualitatively different from that of liquids or gases. In the first place, the compressibility is, as a general rule, less, as is to be expected. As far as I know, there is no exception to the rule that the compressibility of a substance in the solid phase is less than that of its own melt; this is true for normal substances which contract on freezing, and also true for water and bismuth which expand on freezing, and for which the contrary might be expected. It is thus evident that the lattice structure of itself imparts a certain stiffness foreign to the liquid. In the second place, the initial domain of high compressibility followed by very much lower compressibility, which is characteristic of liquids, is much less prominent in solids, the compressibility of which drops off comparatively little at high pressures. It is therefore probable that by far the larger part of the compression of a solid has its origin in the compression of its atoms. A striking example of this is caesium, the atom of which is highly complicated, and the compressibility of which is greater than that of any other metallic element. In Fig. 8 the volume of Cs is plotted against pressure and for comparison the volume of ether, the most compressible organic liquid. The decrease of volume of ether under the first thousand kilograms is nearly twice that of Cs, but the compressibility of Cs persists at high pressures, so that at 12,000 kg. the total volume decrement of

Cs has become very nearly as large as that of ether, and its actual compressibility is materially larger than that of ether.

As a general rule the compressibility of solids decreases at high pressures by amounts which are greater the greater the compressibility, as might be expected, but there are exceptions. The compressibility of pure quartz glass,  $\text{SiO}_2$ , and a number of compound glasses in which the content of  $\text{SiO}_2$  is high, increases with increasing pressure by an amount far beyond experimental error. It has sometimes been thought that molecular stability demands that the compressibility becomes less as the volume becomes less, but this conclusion evidently rests on an incomplete analysis. I have recently found the same anomaly, that is, compressibility increasing with increasing pressure, in the element cerium. The behaviour of potas-

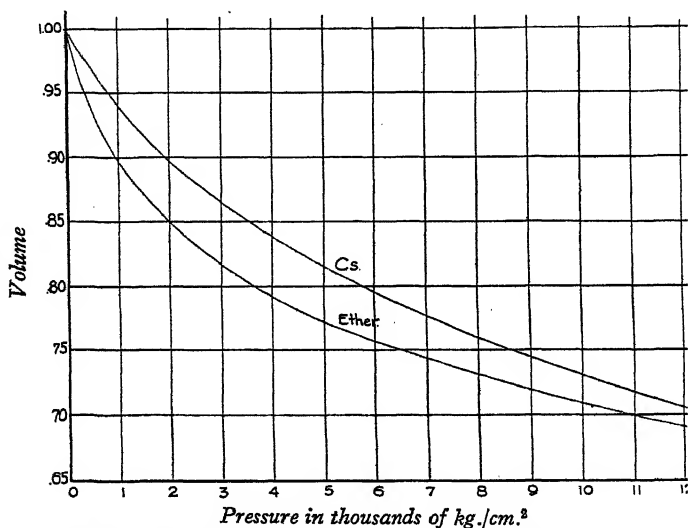


Fig. 8. The volume of ether and  $\text{CS}_2$  as a function of pressure.

sium is also highly significant in this respect when compared with that of the other alkali metals. Fig. 9 shows that the compressibility of potassium drops off with increasing pressure much less than that of Rb or Cs, so that although initially the compressibility of Cs, for example, is nearly twice as great as that of K, at 12,000 kg. it has become considerably less. The persistence of compressibility of K is to be connected with the abnormally loose structure of the atom of K, which is shown by the fact that if the atomic volume of the alkali metals is plotted against atomic number, the volume of K is abnormally high. It is interesting, and probably of considerable significance, that at high pressures in the case of K there is a reversal in the direction of a simple function of the compressibility, which we do not need to explicitly define for our immediate purpose, of such a character that this function starts to approach the value which it would have if K were a perfect gas produced by the disintegration of its atoms into their component electrons and protons.

Of particular significance is the effect of pressure on single crystals. Only in cubic crystals is the change of volume under hydrostatic pressure the same in every

direction, so that to determine completely the effect of pressure on the volume of single crystals the linear compressibility must be measured in several directions. A large number of crystals have been studied from this point of view, and also the variation under pressure of electrical properties in different directions has been measured. The results are too numerous and complex to attempt to summarise here, except to state that the linear compressibility may vary much more with direction than might be expected from the difference of atomic spacing in different directions. Thus the linear compressibility of Zn parallel to the hexagonal axis is seven times as great as at right angles, whereas the ratio of the atomic spacing in the two directions is only 7 per cent. different from that for spherical atoms in normal hexagonal piling, and in fact the spacing is compressed along the axis,

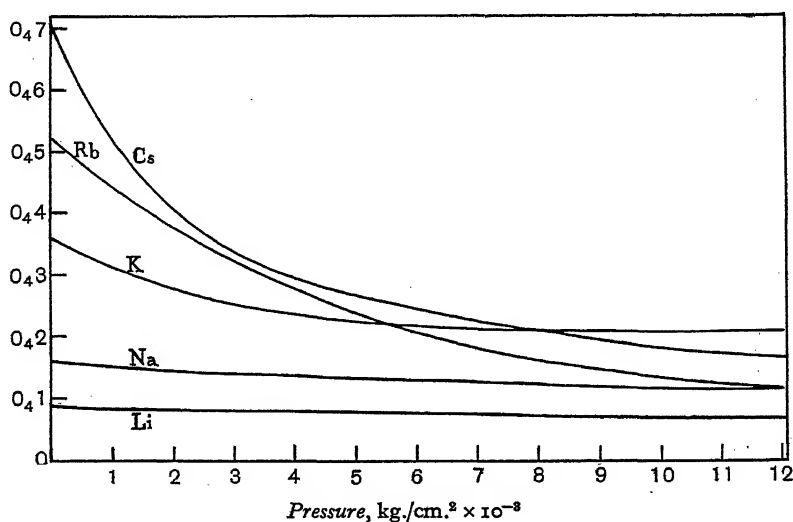


Fig. 9. The instantaneous compressibilities,  $\frac{1}{v} \left( \frac{\partial v}{\partial p} \right)_T$ , at 0° C. of the five alkali metals as a function of pressure.

while the compressibility is greater along the axis. The behaviour of tellurium is highly unusual, in that there is negative compressibility along the trigonal axis; that is, when exposed to hydrostatic pressure a crystal of Te expands in the direction of the axis. It is difficult to believe that effects of this kind can be explained in terms of atoms with spherical symmetry.

Perhaps the simplest of all crystals are the alkali halides. The compressibility of most of these has been measured by Slater up to pressures so high that good values could be found for the change of compressibility with pressure. This effect is at present beyond the reach of theory; although several theories have been proposed which give fairly good values for the initial compressibility, they all give changes of compressibility with pressure which are wide of the mark.

Next in simplicity after changes of volume come perhaps the changes of state produced by high pressure. We have to consider only the phenomena of change



natural of these, based on pure analogy with the critical phenomena between liquid and gas, was that there is a similar critical point between liquid and solid. Another idea prominently advocated by Tammann was that there is a maximum melting temperature, above which a substance is capable of existence only in the liquid phase, no matter how high the pressure. Experiment, however, seems favourable to neither of these points of view, for measurements on nearly forty substances up to 12,000 kg. and on water up to 21,000 kg. show that if either of these two possibilities ever occur, there must be a complete reversal of the universal trends in the experimental range of pressure. All melting curves, whether rising as is normal, or falling like those of water and bismuth, are concave toward the pressure axis. Furthermore, the difference of volume between liquid and solid plotted against melting pressure gives a curve convex toward the pressure axis, and the slope,  $dt/dp$ , of the melting curve plotted against temperature, gives a curve convex toward the temperature axis. A little consideration will show that these universal features demand that there can be neither critical point nor maximum. So far as I can see, there is no reason to think that the melting temperature may not be raised indefinitely by the application of sufficiently great pressure, but the rate at which the temperature is raised by a definite increment of pressure becomes continually less as the pressure becomes higher.

The phenomena of polymorphic transition from one crystalline phase to another show, on the other hand, no such regularities. A number of examples of the phase diagrams of polymorphic substances are shown in Figs. 10 and 11. One of the most interesting of these is that of water which is capable of existence in at least five solid forms under the proper conditions of temperature and pressure. The modifications called II and III in the diagram were first found by Tammann. Of the five modifications, ordinary ice is the only one which is less dense than the liquid, and therefore the only one whose melting temperature is depressed by increasing pressure. Camphor, with six modifications, is the only substance hitherto investigated with more modifications than water.  $\text{NH}_4\text{NO}_3$  has five modifications, like water, in the ordinary temperature range, but at low temperatures there is another modification which there is some reason to think is merely one of the high temperature modifications reappearing at a lower temperature. Inspection shows that there is not the slightest similarity between the diagrams of the different substances. In general the phase diagrams of substances which are closely related are much less similar than their chemical similarity might lead one to expect. The diagrams of  $\text{CCl}_4$  and  $\text{CBr}_4$  are a case in point.

The only generalisation that can be made with regard to all these polymorphic changes is that there seems never to be a critical point between two different crystal modifications. This means that continuous transition from one space lattice to another never occurs, as seems natural enough. Apart from this, the most varied sorts of behaviour are possible. There are a comparatively large number of transition curves of the ice type, that is, those in which the modification stable at the higher temperature has the smaller volume, so that the transition temperature decreases with rising pressure. The transition curves may be either concave or



convex toward the pressure axis. They may have vertical tangents with either maximum or minimum pressures, and one example is known ( $\text{HgI}_2$ ) of a horizontal tangent with maximum temperature. The mere existence of curves with horizontal or vertical tangents is of significance. At a horizontal tangent, the transition occurs with no volume change but with a finite latent heat; on the high-pressure

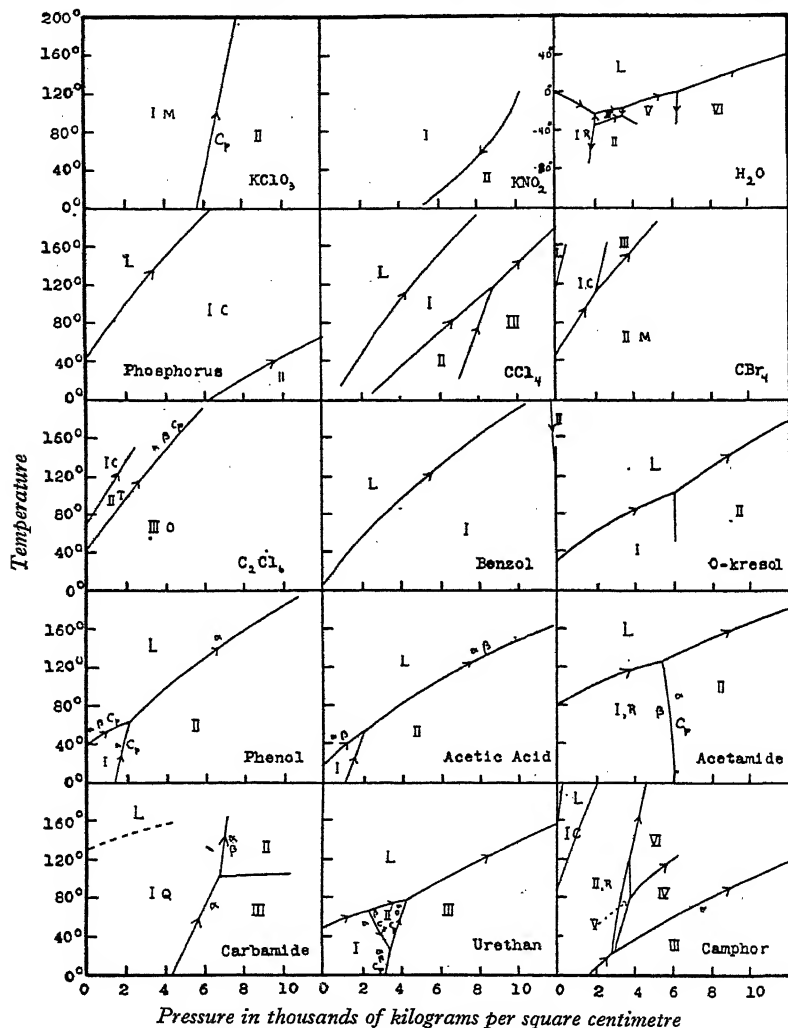


Fig. 11. More phase diagrams, similar to those of Fig. 10.

side of such a horizontal tangent the phase which has the larger volume has the smaller compressibility, a somewhat paradoxical effect. Similarly, at a vertical tangent the transition occurs with no thermal effect, but a finite change of volume; on the low-temperature side of such a vertical tangent the phase stable at the higher temperature has the lower specific heat, again paradoxical.

In addition to the information shown in the diagrams I have in a number of cases been able to measure the difference of compressibility between different

polymorphic forms of the same substance. The surprising result is that in the majority of cases that one of two phases which has the larger volume and which therefore is stable at the lower pressure is the less compressible. It is also true in general that the phase of larger volume has the higher crystalline symmetry. It seems as if the molecules or atoms have some internal structure analogous in some respects to a framework of high symmetry and rigidity, such that at low pressures, where the intensity of the external forces is low enough to permit that the natural arrangement be assumed, the molecules take an arrangement of high symmetry and low compressibility, with the projecting parts of the frameworks of different atoms in register with each other, but at high pressures the natural forces are overcome, the frameworks are pushed out of register, and the system collapses to an arrangement of smaller volume, of lower symmetry, and, because the frameworks are the most rigid part of the molecule, of greater compressibility. I doubt whether the complicated facts of polymorphism, or of the volume relations in liquid, can ever be explained in terms of simple central forces between atoms, although such an explanation is all that has hitherto been attempted, and in spite of the partial justification which such an explanation has lately received from the results of wave mechanics applied to simple systems.

It would appear, then, that a study of polymorphic behaviour gives a very delicate method of analysing the properties of matter in bulk, but at present the complications in the way of a theory are rather formidable. A systematic study of this field should start with the simplest systems. Among the series of substances which have been measured under pressure there are two comparatively simple. One of these is the series  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{Br}$ ,  $\text{NH}_4\text{I}$ ; these experience a polymorphic transition with very large volume change, and the lattice structure of the two modifications is known from X-ray studies at atmospheric pressure. The other of the series is  $\text{RbCl}$ ,  $\text{RbBr}$ ,  $\text{RbI}$ ; the pressure of the transition is in the neighbourhood of 5000 kg., so that a direct X-ray determination of the lattice structure of the high pressure modification has not as yet been possible, but other considerations make it very probable that it is the same body centred cubic type as  $\text{CsCl}$ . No adequate explanation has yet been given of the occurrence of these two types of lattice in the alkali halide series, but enough has been done to show that the type of lattice which has the minimum free energy may be very sensitive to slight changes in the character of the interatomic forces.

Consider next the effect of pressure on electrical resistance. Out of 48 pure metals which have been measured, the resistance of 39 decreases under hydrostatic pressure by amounts varying with the character of the metal from 1 per cent. under 12,000 kg. for Co to 73 per cent. for K. The relation between change of resistance and pressure is not linear, but always the curve of resistance against pressure is convex toward the pressure axis, which means that the effect of a given increment of pressure becomes less at high pressures, as seems natural. In the case of K the initial rate of change is so great that resistance would entirely vanish at a pressure of 5600 kg. if it continued at the initial linear rate. Six or seven of the 48 metals, Li, Ca, Sr, Sb, Bi, the low-pressure modification of Ce, and perhaps Ti, increase in resistance under pressure, and in all these cases the curve of resistance against

pressure is convex toward the pressure axis, just as in the case of the metals with negative coefficient. But now the significance of convexity is that the effect of a given increment of pressure becomes greater at high pressures, which is not to be expected. It is particularly to be noticed that the curvature is such for these two types that the curve for one could be regarded as a prolongation of that of the other, so that it is natural to ask whether the resistance of all metals does not ultimately increase at sufficiently high pressures, the initial difference between different metals being ascribable to different internal pressures. Such an expectation is much strengthened by the discovery of three metals whose resistance does actually pass through a minimum with increasing pressure. The first of these is Cs, which is the most compressible metal, and therefore might be expected to show the effect most easily. The resistance of this at room temperature passes through a minimum of about 0.71 of the initial value between 4000 and 5000 kg. The next is Ba, which stands to the right of Cs in the periodic table, and which has a minimum at 0.97 of the initial resistance at about 8000 kg. Very recently I have found that Rb, which stands above Cs in the periodic table, also has a minimum at 18,000 kg. at 31 per cent. of its initial resistance. Measurements on K show no minimum up to 19,000 kg., but an easy extrapolation by first differences indicates pretty certainly a minimum in the neighbourhood of 24,000 kg. at 18 per cent. of its initial resistance. A similar, but much more uncertain extrapolation of the measurements on Na up to only 12,000 kg. is not unfavourable to the existence of a minimum, but indicates that it occurs at pressures probably considerably higher than 24,000 kg. However, on taking the last step in the series of the alkali metals, all regularity disappears, for the resistance of Li increases from the start with increase of pressure. In Fig. 12 the resistance under pressure of the alkali metals is shown. Furthermore, on passing across to the second column in the periodic table, the irregularities are more striking than the regularities. The resistance of Be decreases under pressure against the increase of Li, Mg decreases as does also Na, but Ca increases against the decrease of K, Sr increases against the decrease of Rb and its increase is greater than that of any other metal, while finally Ba has a minimum as does also Cs, but the whole scale of the pressure effects on Ba is very much smaller than on either Cs or Sr.

It is thus evident that in spite of the extreme simplicity of the change in the lattice structure produced by pressure, the effects of pressure on resistance are complicated, much more complicated than the effects of temperature, for example. I do not believe that any adequate explanation has yet been offered of the effects of pressure on resistance, even by the new wave mechanics. A consideration of the pressure effects makes it fairly certain, however, that the mechanism must be much more complicated than the pure temperature effects would lead us to expect. Particularly, the occurrence of a minimum resistance is suggestive; nearly always a minimum property involves the action of at least two mechanisms, which to a certain extent play against each other.

In addition to the effect of pressure on the electrical conductivity of pure metals, its effect on a number of binary alloys of metals has been measured. Examples are rather frequent here of a positive pressure coefficient of resistance.

One universal generalisation applies to all the measurements yet made on the pressure coefficient of alloys, both by other observers and myself, namely, that the initial effect of adding a small amount of foreign metal to a pure metal is to increase algebraically the pressure coefficient. That is, if the coefficient is initially negative, as it is in the majority of cases, adding a foreign metal makes the coefficient smaller numerically, while if the coefficient is initially positive, it becomes still more positive on addition of another metal. This is capable of a simple geometrical interpretation consistent with the wave mechanics picture of electrical resistance as arising from the scattering of electron waves by irregularities in the atomic structure. For, in addition to the irregularities in the lattice structure of a pure metal

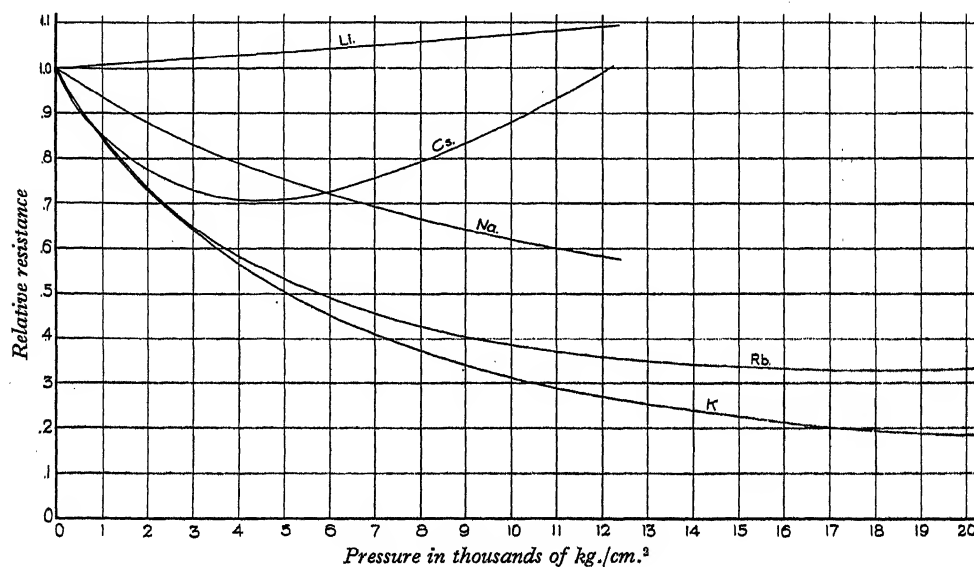


Fig. 12. The relative resistances under pressure of the five alkali metals.

due to temperature agitation, there must in general be irregularity of a purely geometrical character when a foreign metal is introduced, arising from the unequal sizes of the two sorts of atoms. The geometrical discrepancy between the two different sorts of atoms is accentuated as they are pushed into closer contact by pressure, so that the scattering of the electron waves arising from this effect increases, and the pressure coefficient becomes more strongly positive.

The thermal conductivity of metals is also recognised to be an electrical phenomenon, as proved by the universal value of the Wiedemann-Franz ratio. The effect of pressure up to 12,000 kg. has been measured on the thermal conductivity of 11 metals. The measurement is much more difficult to make than of resistance, and the results are not so accurate. Of the 11 metals, the thermal conductivity of 5 increases under pressure and that of 6 decreases. In only two cases does the Wiedemann-Franz ratio increase under pressure, and in the remaining 9 cases it decreases by amounts varying up to 15 per cent. for Ni at

12,000 kg. Since the Wiedemann-Franz ratio varies with pressure, it is obvious that the connection between electrical and thermal conductivity cannot be the universal and simple one of the original theory of Drude. A consideration of the contribution to the thermal conductivity by the atoms as distinguished from the electrons seems to offer a possibility of explaining at least part of the discrepancy, and would suggest that the contribution made by the atoms may be larger than often supposed.

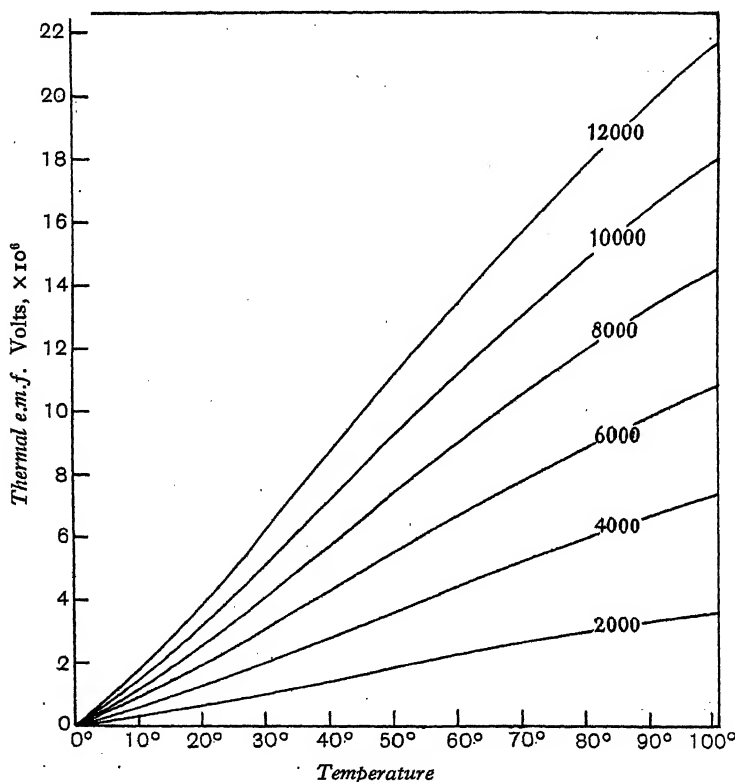


Fig. 13. Thermal e.m.f. of a couple composed of one branch of uncompressed pure platinum, with the other branch composed of the same metal compressed to the pressure in kg./cm.<sup>3</sup> indicated on the curves, the junctions being at 0° C. and the temperature plotted as abscissa.

Thermal e.m.f. is another electrical property that can be measured under pressure without too great difficulty. The effects are not small, for the thermal e.m.f. of a couple composed of a metal in the uncompressed state and the same metal compressed approaches the order of magnitude of the thermal e.m.f. of couples composed of ordinary dissimilar metals. For example, the thermal e.m.f. of a couple composed of Zn uncompressed and compressed to 12,000 kg., with its two junctions at 0° and 100°, is one-third as great as that of a couple of uncompressed Zn and Pb between the same temperature limits.

The effects of pressure on thermal e.m.f. may be exceedingly complicated and vary greatly from one metal to another, as Figs. 13 and 14 show. In general the

effect of pressure on Peltier and Thomson heats is positive, that is, the positive current absorbs heat in flowing from uncompressed to compressed metal, and the Thomson heat absorbed in passing from a low to a high temperature is greater in the compressed than in the uncompressed metal, but the irregularities are much greater than the irregularities in the resistance effects and occur in unexpected places, the irregularity of thermal e.m.f. being greatest for Sn, Fe, and Al, metals without special distinction in other respects under pressure. Just as in the case of resistance phenomena, these complicated effects indicate a complicated mechanism, certainly more complicated than contemplated in any theory yet proposed. There is no discoverable parallelism between the effects of pressure on resistance and on

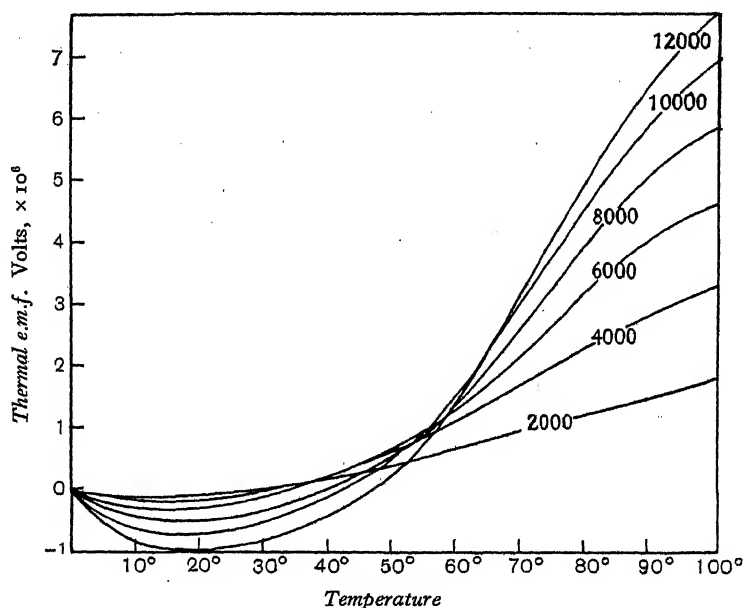


Fig. 14. Thermal e.m.f. of a couple composed of one branch of uncompressed pure iron, with the other branch composed of the same metal compressed to the pressure in kg./cm.<sup>2</sup> indicated on the curves, the junctions being at 0° C. and the temperature plotted as abscissae.

thermal e.m.f., from which one may perhaps draw the conclusion that essentially different aspects of the electron mechanism are responsible for thermoelectric phenomena, and the phenomena of resistance.

Passing now to another group of phenomena, the thermal conductivity of 15 liquids has been measured to 12,000 kg. The effect is to increase thermal conductivity by fairly large amounts, the factor of increase varying from 1.50 for water, the least compressible of the substances measured, to 2.74 for normal pentane, approximately the most compressible. It is very suggestive that this increase runs roughly parallel with the increase in the velocity of sound under pressure, as calculated from the change of density and the compressibility. I have found a very simple relation, suggested by this fact, for the thermal conductivity of liquids, namely,  $k = \alpha v \delta^{-2}$ . Here  $k$  is thermal conductivity in absolute units,  $\alpha$  is the

molecular gas constant  $2.02 \times 10^{-16}$ ,  $v$  the velocity of sound, and  $\delta$  the mean distance of separation of the molecules in the liquid, assuming them piled in simple cubic array. The formula represents with considerable success the thermal conductivity of normal liquids, of water, which is abnormal in so many respects, and also of non-crystalline solids, such as glass or hard rubber.

In gases the phenomena of viscosity are closely connected with those of thermal conductivity, but in liquids the difference in behaviour of the temperature coefficients of thermal conductivity and viscosity makes it highly probable that the mechanisms of the two effects are different. This view receives strong support from the pressure effect on viscosity, which has been measured for 43 liquids. In all cases, except the abnormal one of water and then only over a limited range of pressure and temperature, viscosity increases under pressure, and by amounts varying enormously from substance to substance. The factor of variation under 12,000 kg. is 1.33 for mercury, and  $10^7$  for eugenol ( $C_3H_5.C_6H_3.OH.OCH_3$ ). In fact, the pressure effect on viscosity and its variation from substance to substance is much greater than any other known pressure effect. Viscosity increases geometrically with pressure, that is, the logarithm of viscosity is approximately a linear function of pressure. There is a very close correlation between the magnitude of the pressure effect and the complexity of the molecular structure, the pressure coefficient being least for monatomic Hg and greatest for complicated organic substances like eugenol. It is evident that no purely kinetic mechanism of viscosity, such as we have in gases, is competent to explain such enormously large effects. There would seem to be little question that a large part of the viscosity of a liquid is purely mechanical in origin, arising from the jamming together or interlocking of the molecules. Such a mechanism is consistent with the very large pressure effects, and the enormous variations of this effect with molecular complexity.

Finally, I may mention an investigation not yet finished on the effect of pressure on the shearing modulus or rigidity of solids. Hitherto the only elastic constant which has been measured under pressure is compressibility, but there would be considerable interest in determining how pressure affects all the constants. Unfortunately this is a matter of great experimental difficulty, and up to the present I have been able to measure the effect of pressure only on the shearing modulus of several isotropic substances. The rigidity of Fe increases under pressure, as would be expected, the increase being about 2.5 per cent. for 12,000 kg. The rigidity of glass, on the other hand, decreases by amounts varying with the composition from 0.7 per cent. to 11 per cent. for 12,000 kg. The effect is largest for those glasses which have the abnormal increase of compressibility with pressure, as might be expected. By combining this change in the shearing modulus with the known changes in density, it may be calculated that the velocity of a wave of shear decreases under 12,000 kg. by amounts varying from 2 to 6 per cent., a fact of some possible geological interest. By combining the pressure coefficient of rigidity with the pressure coefficient of compressibility, the effect of pressure on Young's modulus may be found; this may increase or decrease under pressure depending on the composition of the glass, by amounts varying from +2.5 per cent. to -10 per cent. under 12,000 kg.

# THE SPECTRUM OF TREBLY-IONISED THALLIUM

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**ABSTRACT.** Using the measurements made by Carroll of the vacuum spark spectrum of thallium, combinations of the triad of triplet and singlet F, D, P terms of the  $d^9p$  configuration of Tl IV with the deeper  $^3D$  and  $^1D$  of the  $d^9s$  state have been found. Justification of the scheme is sought by comparison with similarly constituted spectra.

## § 1. INTRODUCTION

WHILE the arc spectrum of thallium has long been known to consist of a well-developed doublet system, investigations for series relationships among the enhanced lines in the spark have been few. The first attempt at the analysis of the spark lines was that of Carroll\*, who made extensive measurements of the "hot spark" spectrum of the element and indicated the chief doublets of Tl III. In a previous paper† the present writer, working in collaboration with Prof. Narayan and Mr A. S. Rao, has shown that some of the more easily excitable lines of the thallium spark form a triplet system characterising the spectrum of Tl II. The resonance and second ionisation potentials were found to be 6.47 and 20.3 volts respectively.

The measurements of Carroll contain strong unclassified lines in the extreme ultra-violet and it is believed that many of these may be due to the higher stages of ionisation of the element, as the method of excitation used by Carroll was particularly favourable for their production. The present paper shows that some of these lines can be grouped into a triplet system involving the deeper levels of trebly-ionised thallium. Evidence of the correctness of the identification is afforded by comparison with related spectra.

## § 2. THEORETICAL CONSIDERATIONS

The trebly-ionised atom of thallium contains a group of ten electrons outside the inner completed shells. Recent work of Shenstone‡, Laporte and Lang§ McLennan|| and others¶ on the spectra of Ni-, Pd- and Pt-like atoms shows that

\* *Phil. Trans. (London)*, A, 225, 357 (1926).

† *Ind. Journ. Phys.* 2, 467 (1928). Later McLennan and others, *Phil. Trans. R.S.C. Sect. 3*, 22 241 (1928), and also Smith, *Proc. Nat. Acad. Sci.* 14, 951 (1928), came to identical conclusions.

‡ (Cu II), *Phys. Rev.* 29, 380 (1927); (Ag II), 31, 317 (1928); also Mazumdar, *Ind. Journ. Phys.* (1928).

§ (Zn III), *Phys. Rev.* 30, 378 (1927); (Ga IV and Ge V), *Phys. Rev.* 31, 748 (1927).

|| (Ag II, Cd III, Au II, Hg III), *Trans. R.S.C. Sect. 3*, 22, 1, 45, 103 (1927) and 22, 247 (1928).

¶ (Cd III, In IV), *Phys. Rev.* 31, 776 (1927); (Sn V), *Proc. Nat. Acad. Sci.* 14, 345 (1928).



in such a ten-electron system the important configurations producing the optical spectrum are those built upon the normal state of the preceding ion, which is a  $^3D$  term arising from nine equivalent  $n_s$  electrons. The terms from such a configuration are, according to Hund's theory, given in the following table:

Table 1: Scheme of terms

5 <sub>1</sub> 5 <sub>2</sub> 5 <sub>3</sub> 5 <sub>4</sub>	6 <sub>1</sub> 6 <sub>2</sub> 6 <sub>3</sub>	Term prefix	Terms
2 6 10		5 <i>d</i>	$^1S$
2 6 9	1	6 <i>s</i>	$^3D$ $^1D$
2 6 9		6 <i>p</i>	$^3F$ $^3D$ $^3P$ $^1F$ $^1D$ $^1P$
2 6 9		6 <i>d</i>	$\begin{Bmatrix} ^3G \\ ^1G \end{Bmatrix}$ $^3F$ $^3D$ $^3P$ $^3S$ $^1F$ $^1D$ $^1P$ $^1S$

The dashing of the terms is found unnecessary as, according to the notation adopted by Prof. Fowler, the term prefix itself determines the combinations.

### § 3. RESULTS

The results of the analysis of Tl IV are presented in Table 2 where frequencies are calculated from Carroll's list of wave-lengths. Term values are arbitrary and are found by assuming  $^3D_3$  to be zero. Only combinations between the triad of triplet and singlet F, D, P terms of the  $d^9p$  state with the deeper  $^3D$  and  $^1D$  of  $d^9s$  have been found in this investigation. The three possible combination lines of the 6*p* terms with the deepest 5*d*  $^1S$  are expected to lie far outside the region investigated by Carroll and could not be located.

Table 2: Multiplets of Tl IV

6 <i>p</i> \ 6 <i>s</i>	$^3D_3$ 0 3586	$^3D_2$ 3586 15028	$^3D_1$ 18614 3049	$^1D_2$ 21663
$^3P_2 = 72582$ 19854	72582 (7)	68996 (5)	[53968]	50901 (3) <i>d</i> ?
$P_1 = 92436$ 16314	—	88848 (4)	[73820]	70775 (5)
$P_0 = 108750$	—	—	90136 (4)	—
$^3F_4 = 90942$ — 16161	90942 (6)	—	—	—
$F_3 = 74781$ 20488	74784 (4)	71195 (8)	—	53115 (5)
$F_2 = 95269$	[95270]	91684 (4)	76654 (3)	73606 (5)
$^3D_3 = 97009$ — 5650	97006 (3)	93416 ( <i>x</i> )	—	75362 (0)
$D_2 = 91359$ 23722	91353 (0)	87773 (5)	72747 (5)	69701 (6)
$D_1 = 115081$	—	[111497]	96469 (3)	93416 (4 - <i>x</i> )
$^1F_3 = 109822$	—	—	—	88159 (4)
$^1P_1 = 110975$	—	—	92363 (4)	89309 (2)
$^1D_2 = 113168$	—	—	94557 (2)	91500 (2)

[ ] Bracketed values are calculated; the lines are expected to be faint.

While there seems to be no doubt as to the identification of the 6*p* triplet terms, as succeeding pages will show, there may be some uncertainty with regard to the

singlets  $6p\ ^1F\ ^1P\ ^1D$ . They have been located mainly by consideration of the estimated positions of the lines and the occurrence of the separation 3049, equal to  $6s\ ^3D_1-6s\ ^1D_2$ , and they lack further check as their combinations with  $6s\ ^3D_{32}$  fall far outside Carroll's list. The vacuum spark spectrum of thallium must be investigated below  $\lambda\ 900$  before these levels can be established with certainty. The levels  $^3P_0$  and  $^3F_4$  had to be fixed only by a single transition in each case, but alternative choice\* was found unsatisfactory. The line  $\nu\ 93416$  occurs twice in the table; the intensity of the line, however, supports the assignments. It is further significant to observe that the combination  $4s\ ^3D_2-4p\ ^3D_3$  is either faint or absent in Ni I-like spectra.

An interesting point as regards the intensities of the lines deserves mention. While it may not be safe to conclude from visual estimates of intensities of such widely separated lines, there appears still to be in Tl IV a definite increase in intensities of the intercombination lines relative to those of triplet-triplet and singlet-singlet combinations. This feature was observed also by Mack, Laporte and Lang in Ga IV and Ge V.

#### § 4. COMPARISON WITH RELATED SPECTRA

Apart from the recurrence of constant frequency-differences and the location of intercombination lines, a valuable check on the identification of the members is afforded by a comparison with spectra of related elements. Our knowledge of the spectra of Au II, Hg III and Ga IV, In IV permits of such a comparison.

Laporte and Lang have shown that the application of the relativity laws to iso-electronic spectra, successfully employed by Millikan and Bowen in the case of "normal" spectra, can be fairly utilised for the prediction and location of line groups which occur in spectra with a large number of electrons, and involve separations between sub-levels large compared with those between different terms.

The regular doublet sequence is shown in Table 3.

Table 3: Regular doublet sequence

(At. No.) Element	$6s\ ^3D_3-6s\ ^3D_1$ ( $\Delta\nu$ )	$\sqrt[4]{\frac{\Delta\nu}{0.00776}}$	$s$	$\Delta s$
78 Pt I	10132	33.8	44.2	
79 Au II	12728	35.8	43.2	1.0
80 Hg III	15556	37.6	42.4	0.8
81 Tl IV	18613	39.3	41.7	0.7

The values of the screening constant ( $s$ ) exhibit the familiar slow decrease with increasing atomic number.

The irregular doublet sequence is indicated in Table 4, where the mean of the frequencies of the lines in each multiplet is taken for purposes of comparison.

\*  $\nu\ 92618\ (6)$  might be suggested as equally probable for  $^3D_3-^3F_4$ .

Table 4: Irregular doublet sequence

Element	(6s <sup>3</sup> D-6p <sup>3</sup> F) Diff.	(6s <sup>3</sup> D-6p <sup>3</sup> P) Diff.	(6s <sup>3</sup> D-6p <sup>3</sup> D) Diff.
Au II	54004	47494	57423
Hg III	68835	—	75887
Tl IV	83421	74725	92894
	14831		18464
	14586		17007

Table 5 gives the separations of the various terms in the iso-electronic spectra Au II, Hg III, Tl IV on the one hand and in the spectra of the elements Ga IV, In IV and Tl IV of the same chemical group on the other.

Table 5: Term intervals

Term	Au II	Hg III	Tl IV	In IV	Ga IV
6s <sup>3</sup> D <sub>3</sub>	2602	3179	3586	2197	1455
D <sub>2</sub>	10125	12377	15028	4912	2120
D <sub>1</sub>					
6p <sup>3</sup> P <sub>2</sub>	10351	15057	19854	6658	3081
P <sub>1</sub>	9210	—	16314	4395	1820
P <sub>0</sub>					
<sup>3</sup> F <sub>4</sub>	-7492	-12366	-16161	-4452	-1271
F <sub>3</sub>	11656	15300	20488	8651	2358
F <sub>2</sub>					
<sup>3</sup> D <sub>3</sub>	-1613	-3052	-5650	-3824	636
D <sub>2</sub>	12529	17928	23722	9522	3080
D <sub>1</sub>					

A general variation of the intervals between the terms of these spectra is obvious. But, as is expected, the variation is more regular and progressive in the sequence of spectra Au II, Hg III, Tl IV, than in that of Ga IV, In IV, Tl IV.

The relative values of singlet and triplet terms of a given configuration present considerable interest. While in Ni- and Pd-like spectra, and also in Au II, 6p<sup>3</sup>D<sub>1</sub> is deeper than 6p<sup>1</sup>D<sub>2</sub>, the reverse is the case in Hg III, and if the identification of 6p<sup>1</sup>D<sub>2</sub> in Tl IV proves correct, this feature recurs in this spectrum also. The partial inversion of 6p<sup>3</sup>F and <sup>3</sup>D and the complete inversion of 6p<sup>3</sup>P and 6s<sup>3</sup>D are analogous to those of Au II and Hg III.

The ratio of the separations  $\{(ms) {}^3D_2 - {}^3D_3\} / \{{}^3D_1 - {}^3D_3\}$  is shown in the case of these ten electron systems in Table 6, which is an extension of a table given by Mack, Laporte and Lang\*. They have shown that the progressive decrease of this ratio from Ni I to Ge V and the marked decrease from Ag II to Sn V are evidences against the following correlation of limits by Hund:

$$d^9s {}^3D_3 {}^1D_2 \rightarrow d^9 {}^3D_{5/2}$$

$${}^3D_2 {}^3D_1 \rightarrow {}^2D_{3/2}.$$

A similar marked decrease of this ratio occurs also in Au II to Tl IV. The variations of the levels, in these spectra, as the nuclear charge increases, indicates that the limits for the levels <sup>1</sup>D<sub>2</sub> and <sup>3</sup>D<sub>2</sub> should be interchanged.

\* *loc. cit.* p. 763.

Table 6: Ratio of separations

Ni I 0.448	Cu II 0.444	Zn III 0.428	Ga IV 0.407	Ge V 0.384
Pd I 0.337	Ag II 0.345	Cd III 0.330	In IV 0.309	Sn V 0.287
Pt I 0.077	Au II 0.257	Hg III 0.204	Tl IV 0.193	Pb V —

Finally, the lines of thallium classified in this investigation are collected in Table 7 for the sake of convenience.

Table 7: List of the lines

$\lambda$ (int.)	$\nu$ (vac.)	Classification
1964.6 (3)	50901	$6s\ ^1D_2-6p\ ^3P_2$
1882.7 (5)	53115	$^1D_2-^3F_3$
—	[53968]	$^3D_1-^3P_2$
1449.37 (5)	68996	$^3D_2-^3P_2$
34.71 (6)	69701	$^1D_2-^3D_2$
12.93 (5)	70775	$^1D_2-^3P_1$
04.60 (8)	71195	$^3D_2-^3F_3$
1377.75 (7)	72582	$^3D_3-^3P_2$
74.62 (5)	72747	$^3D_1-^3D_2$
58.58 (5)	73606	$^1D_2-^3F_2$
—	[73820]	$^3D_1-^3P_1$
37.19 (4)	74784	$^3D_3-^3F_3$
26.93 (0)	75362	$^1D_2-^3D_3$
04.55 (3)	76654	$^3D_1-^3F_2$
1139.30 (5)	87773	$^3D_2-^3D_2$
25.52 (4)	88848	$^3D_2-^3P_1$
19.71 (2)	89309	$^1D_2-^1P_1$
09.43 (4)	90136	$^3D_1-^3P_0$
1099.60 (6)	90942	$^3D_3-^3F_4$
94.65 (0)	91353	$^3D_3-^3D_2$
92.90 (2)	91500	$^1D_2-^1D_2$
90.70 (4)	91684	$^3D_2-^3F_2$
70.48 (4)	93416	$^3D_2-^3D_3$ also $^1D_2-^3D_1$
57.56 (2)	94557	$^3D_1-^1D_2$
—	[95270]	$^3D_3-^3F_2$
36.60 (3)	96469	$^3D_1-^3D_1$
30.86 (3)	97006	$^3D_3-^3D_3$
—	[111497]	$^3D_2-^3D_1$

## § 5. ACKNOWLEDGMENT

I wish to express my grateful thanks to Prof. A. Fowler, F.R.S., for his stimulating interest in the work and helpful criticism.

## DISCUSSION

Mr E. W. H. SELWYN: I think that the manner in which Mr Rao has sorted out wave numbers from a list of practically completely unclassified lines, until they represent a useful analysis, is much to be admired.

# THE ELASTIC PROPERTIES OF THICK CYLINDRICAL SHELLS UNDER INTERNAL PRESSURE

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**ABSTRACT.** An account is given of an experimental investigation of the usually accepted theory relating to the stresses in a thick cylindrical shell under pressure. The theory is examined in the light of the longitudinal and diametral extensions of a number of steel cylinders which were subjected internally to hydrostatic pressure, the cylinders being closed at the ends by covers secured to the shell itself. Formulae derived from the theory provide a ready means of arriving at the values of the elastic constants  $E$ ,  $\sigma$  and  $K$ . The values of  $E$  and  $\sigma$  were found by pressure experiments and also by direct tension experiments in a lever-testing machine. The results show a discrepancy of about 3 per cent. between the values of the constants thus obtained. The longitudinal extensions in the pressure experiments should give the bulk modulus  $K$ , but the value thus obtained is about 7 per cent. less than the value obtained by calculation from the determinations of  $E$  and  $\sigma$  in direct tension experiments. The author endeavours to explain these discrepancies as being due to the non-isotropic nature of the material, and he shows how on this assumption the values of  $E$  and  $\sigma$  for a lateral direction may be estimated from his results.

The paper gives some information concerning the high-pressure apparatus which was employed, this being designed on the lines suggested by Prof. P. W. Bridgman; a comparison is also made between the working of the roller extensometer developed by Prof. E. H. Lamb and two other extensometers commonly used in engineering laboratories.

## § 1. SYMBOLS USED IN THE TEXT

- $p$ , pressure.
- $q$ , hoop stress.
- $f$ , longitudinal stress.
- $r$ , radius.
- $k$ , ratio of outer diameter to inner diameter of shell.
- $e_2$ , diametral strain.
- $e_3$ , longitudinal strain.
- $E$ , Young's modulus.
- $K$ , bulk modulus.
- $\sigma$ , Poisson's ratio.
- $d$ , mean of diameters of extensometer rollers in inches.
- $L$ , distance from scale to extensometer mirror facing it in cm.
- $l$ , distance between extensometer mirrors in cm.
- $\alpha$ , extensometer scale reading in cm.

## § 2. INTRODUCTION

THE usually accepted theory\* relating to the stresses in thick cylindrical shells under pressure leads to the equations

$$p = A + B/r^2, \quad q = A - B/r^2 \quad \dots\dots(1),$$

in which  $A$  and  $B$  are constants. The theory assumes a perfectly isotropic material, that a cross-section remains plane and generating lines straight after the deformation of the material has taken place, and that the alterations in the radial dimensions of the shell are inappreciable after the application of the pressure.

The values of the constants  $A$  and  $B$  are determined by the conditions at the inner and outer surfaces of the shell. If there is a hydrostatic pressure  $p_0$  acting on the inner surface, whilst the outer surface is at zero pressure, we have

$$A = \frac{r_1^2}{r_2^2 - r_1^2} p_0, \quad B = -\frac{r_1^2 r_2^2}{r_2^2 - r_1^2} p_0 \quad \dots\dots(2),$$

in which  $r_1$  and  $r_2$  are the inner and outer radii of the shell respectively.

If the shell is closed at both ends, the internal pressure  $p_0$  produces in the material a longitudinal stress  $f$ , and  $f \cdot \pi (r_2^2 - r_1^2) = p_0 \pi r_1^2$ ,

$$\text{or} \quad f = \frac{r_1^2}{r_2^2 - r_1^2} p_0 \quad \dots\dots(3).$$

$$\text{But} \quad e_3 = f/E - (\sigma/E) (p + q) \quad \dots\dots(4),$$

and hence from (1), making use of (2) and (3), we have

$$\frac{E}{1 - 2\sigma} \cdot e_3 = \frac{p_0}{k^2 - 1} \quad \dots\dots(5).$$

$$\text{Again, at the outer surface} \quad e_2 = q/E - \sigma f/E \quad \dots\dots(6).$$

Putting in the values of  $q$  and  $f$ , we have

$$e_2 \cdot E/(2 - \sigma) = p_0/(k^2 - 1) \quad \dots\dots(7).$$

From (5) and (7), for the same value of  $p_0$ ,

$$(2 - \sigma)/(1 - 2\sigma) = e_2/e_3 \quad \dots\dots(8).$$

The formulae (5), (7), and (8), if the theory is correct, afford us a means of determining  $E$  and  $\sigma$  directly by extensional measurements.

The object of the present work is to examine the above theory by means of longitudinal and diametral extensional measurements of a thick cylindrical shell subjected internally to hydrostatic pressure, the cylinder being closed at both ends by covers secured to the shell itself. From these measurements the elastic constants  $E$  and  $\sigma$  are calculated according to the theory and are compared with the values determined by measurement of the longitudinal extensions and transverse contractions under tensile stress.

If work of this kind is to be carried out successfully, one must employ a material which from the standpoint of its elasticity is as nearly perfect as possible. It is also essential that the hollow cylinders be made with the greatest care with respect to their inner and outer surfaces being co-axial, and with respect to the generating lines of the surfaces being parallel.

\* Love, *Mathematical Theory of Elasticity* (1928).

For the purpose of the measurement of the longitudinal and diametral strains one must employ extensometers which are designed to measure accurately very small extensions. The longitudinal strains, especially in the case of the thicker shells, are, as indicated by the above theory, very small, much smaller than the corresponding diametral strains. The longitudinal extensometer, while it must be a very sensitive instrument, must also be such that its precision in working is not affected by the disturbance which unavoidably occurs at its points of contact with the cylinder owing to the bulging of the shell.

Measurements by delicate instruments of this kind must of course be taken in a room free from sudden changes of temperature.

For the generation and accurate measurement of the hydrostatic pressure inside the shell special apparatus is necessary. The pressures are high, as great as 15 tons per square inch (2286 atmospheres) if steel cylinders are employed in the investigation. For the measurement of pressures of this magnitude apparatus capable of greater accuracy than a Bourdon pressure gauge is desirable.

### § 3. THE MATERIAL

The thick cylindrical shells were made of high quality steel from four bars supplied by Messrs Thos. Firth and Sons, and the cylinders in the course of making were normalised. The analysis of each bar is shown in Table 1.

Table 1: Analysis of metal bars

Designation of bar	C	Si	Mn	S	P	Ni	Cr
1	0.39	0.22	0.58	0.016	0.012	3.48	0.07
2	0.43	0.28	0.53	0.017	0.029	0.27	—
3	0.28	0.15	0.41	0.018	0.029	0.15	—
4	0.09	0.06	0.28	0.021	0.012	0.27	—

The ultimate tensile strength of these steels after normalising was between 22 and 50 tons per square inch.

Seventeen specimen cylindrical shells were made from the four bars. The shape of each specimen is shown in Fig. 1, and the dimensions, together with the value of  $(k^2 - 1)$  for each, are given in Table 3.

In the making of a specimen every precaution was taken in order to ensure that the inner and outer surfaces were co-axial. The work of drilling the longer specimens was kindly undertaken by Messrs The Birmingham Small Arms Co.

### § 4. THE EXTENSOMETERS

The mirror extensometers, both longitudinal and lateral, developed by Prof. E. H. Lamb\*, are capable of a very fine degree of accuracy, and would appear to be admirably suited to work of this nature. Certain slight modifications were made in the construction of these instruments, and in their method of use in the present investigation.

\* *Engineering*, 119, 207 (1925).

In order to measure the longitudinal extensions of the shorter cylinders under test, an instrument which could deal with the extensions of a 2-in. length of shell was made, the diameters of the rollers being about 0.0625 in. This instrument is seen in position on the thick cylinder under pressure in Fig. 1. It is here seen that between each of the two nuts and the clamp which secures the two parts of the

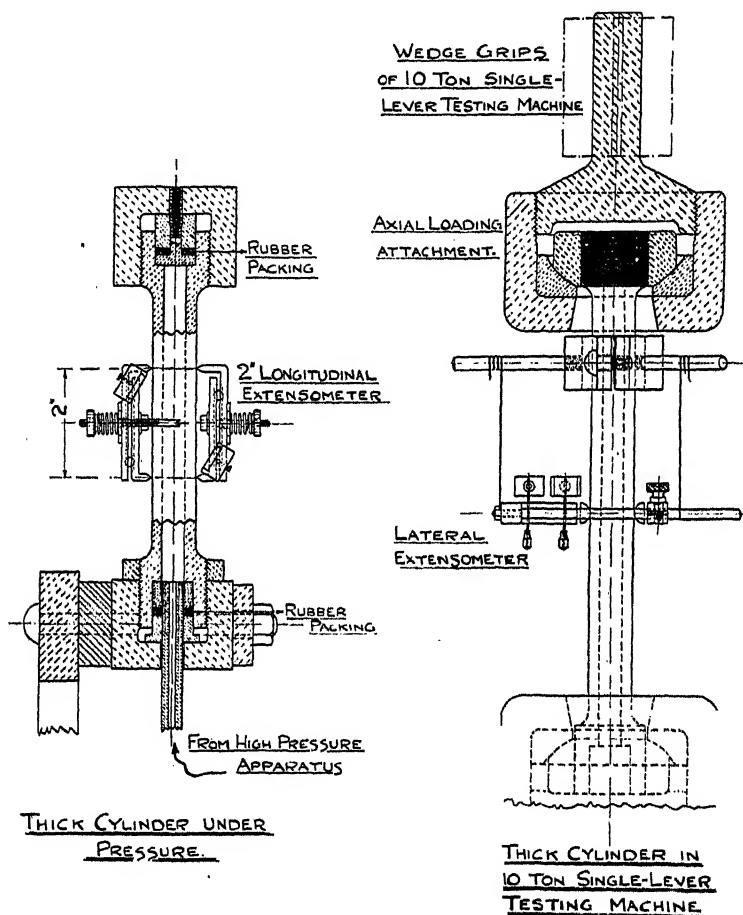


Fig. 1.

extensometer to the cylinder a light spring is inserted. This, by being flexible, takes up the bulge of the shell, and thus the tendency of the left-hand roller to slip rather than to roll between the pair of distance strips is minimised.

Each mirror-holder was balanced rotationally on its roller, and the knob at the other end of the roller was of about the same mass as the mirror-holder. Then, in order to be certain as to the exact distance, nominally 2 in., between the knife-edges, and also to be certain as to the grip of the instrument on the specimen, two fine grooves about 0.002 in. deep were scratched on the surface of the cylinder, and



particular care was taken when setting up the instrument to see that the four points of contact were in these grooves.

In the case of the lateral extensometer an attempt was made to obtain point contact between the instrument and the surface of the specimen by having the "contacts" of semi-cylindrical shape as shown in the right-hand view of the thick cylinder in the 10-ton testing machine (Fig. 1). The extensometer was also supported lightly by three pieces of thin cord. In the pressure experiments these were made fast to a plate attached to the top nut which closed the thick cylinder when under pressure.

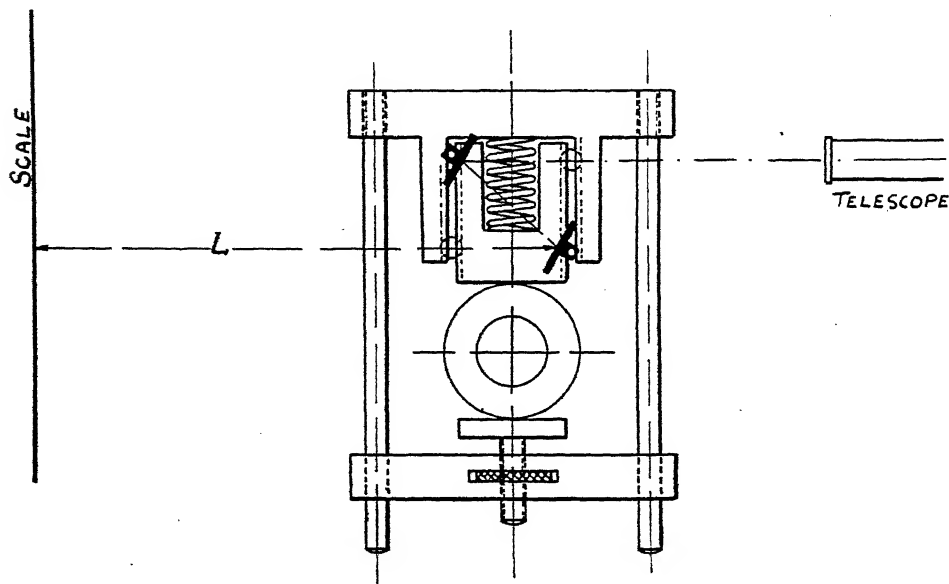


Fig. 2.

The geometry of the optical arrangement is the same for both instruments. Referring to Fig. 2, it is easily proved that the lateral extension of the specimen is equal to  $\frac{d}{4L + 2l} \cdot x$ , and this holds for the longitudinal extensions as measured by means of the 2-in. instrument shown on the left of Fig. 1. The value of  $d$  can be obtained accurately by means of a Newall measuring machine, the values of  $L$  and  $l$  by means of a tape measure, and the scale reading  $x$ , with the help of a good telescope provided with a proper spider-line, can be read accurately to the nearest 0.1 mm. at a distance of 460 cm.

Sudden temperature changes are always a serious difficulty in accurate extensometer work, and so is vibration. For these reasons the work here recorded was carried out in a cellar which was some distance away from machinery and was free from sunlight and draughts.

The effect of placing a screen between the observer and the extensometer was tested. It was found that the rate of rise in temperature, as recorded by a delicate

thermometer placed in the immediate vicinity of the specimen, with the screen in position was less than half what it was without the screen. But it was also found in the course of the investigations that the extensional measurements did not show any appreciable discrepancy between readings taken with and without the screen. The instrument is itself perhaps as good an indication of sudden temperature changes in the room as any sensitive thermometer.

### § 5. THE HIGH-PRESSURE APPARATUS

The high-pressure apparatus was designed and constructed on the lines suggested by Prof. P. W. Bridgman in his various contributions to the *Proceedings of the American Academy*, 44, 47, and 49. It consists of a force-pump, a hydraulic press, and a cylinder in which the high pressures are generated and measured. Two sectional views of the hydraulic press are given in Fig. 3, and a sectional view of the high-pressure cylinder in Fig. 4, and two views of these parts assembled together are to be seen in Fig. 5. The force-pump was made by C. W. Cook, Ltd., and was designed to deliver liquid at pressures up to 5 tons per sq. in. The pump in communication with the  $2\frac{1}{2}$ -inches-diameter piston of the hydraulic press forces a

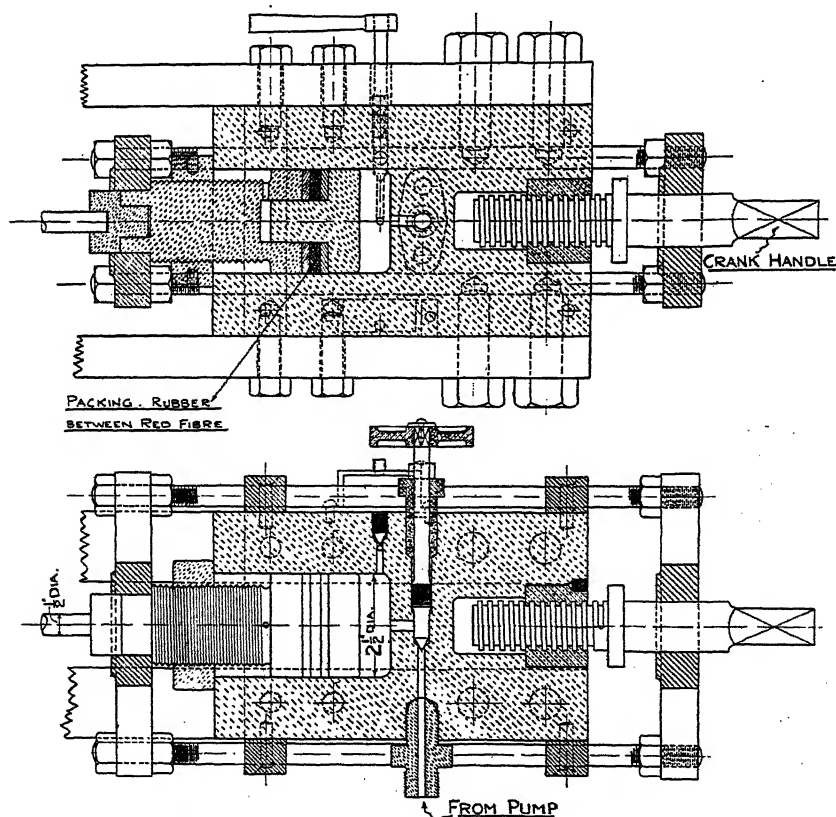


Fig. 3.

$\frac{1}{2}$ -inch-diameter plunger into the high-pressure cylinder. Thus liquid at a pressure of 1 ton per sq. in. from the force-pump acting on the  $2\frac{1}{2}$ -inches-diameter piston of the hydraulic press should generate a pressure of 25 tons per sq. in. in the high-pressure cylinder. Actually, on account of friction, the pressure is somewhat less than this.

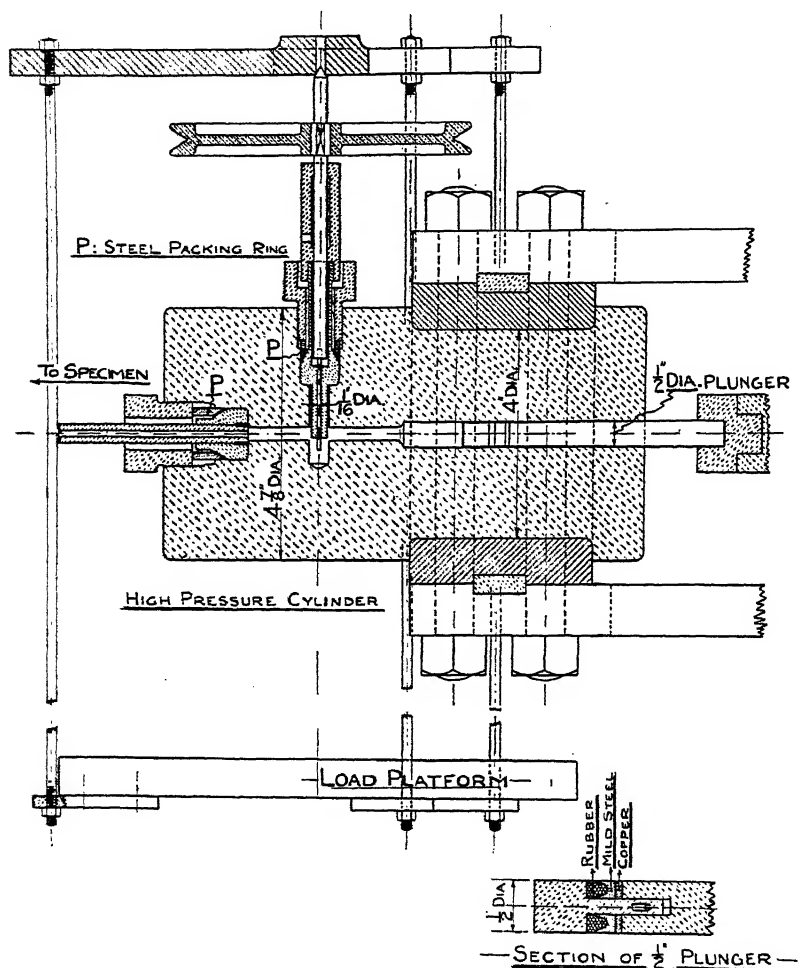


Fig. 4.

The pressure generated in the high-pressure cylinder is measured directly by means of a loaded plunger of diameter 0.0638 in. marked " $\frac{1}{16}$ " Dia." in Fig. 4; and the load is applied to this little plunger by adding weights to a platform which is suspended, in the manner shown, from the top of the spindle carrying the little plunger. To eliminate friction this spindle is rotated by means of an electric motor.

Considerable care was given to the construction of the little plunger and of the fitting which carries it. The plunger was made from a knitting-needle, which was "lapped down" parallel and to the correct size. The hole in which it works was

"lapped out" so that the plunger was of a good fit. Afterwards, when the apparatus had been given a trial under a high pressure, the little plunger was removed, and its diameter within about  $\frac{1}{2}$  in. from its connection to the load spindle was reduced about 0.0002 in. in order to remove the marks of excessive rubbing which it had acquired while under pressure.

The diameter of the little plunger was obtained accurately to within 0.00005 in. by means of a Newall measuring machine.

The liquid employed in the high-pressure cylinder for communicating the pressure to the specimen cylindrical shell was a very viscous mixture of glucose and glycerine. The liquid employed in the hydraulic press was a mixture of glycerine and water.

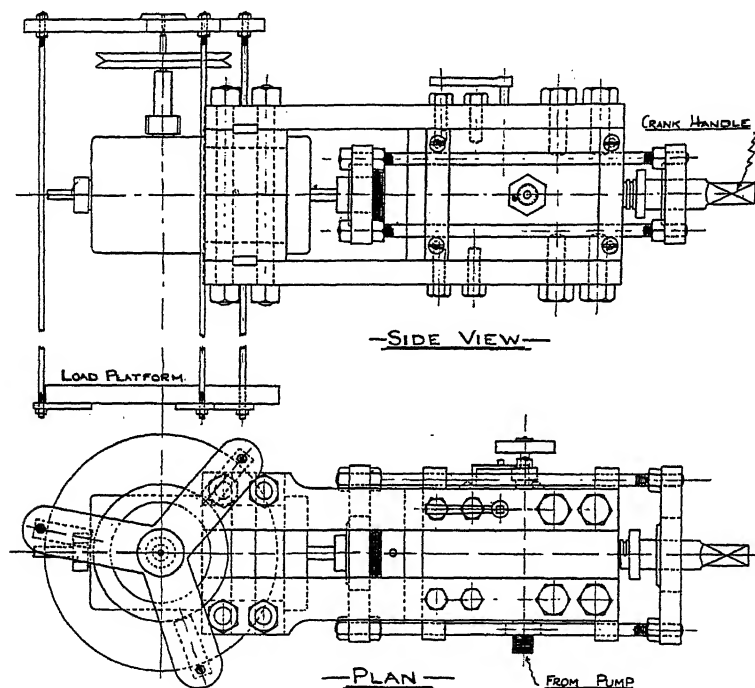


Fig. 5.

The method of packing the  $2\frac{1}{2}$ -inches-diameter piston, and the  $\frac{1}{2}$ -inch-diameter plunger, also the methods adopted for making the various joints in the apparatus are clearly shown in the figures.

All the parts of the apparatus exposed to high pressure were made of special alloy steel of high tensile strength. For example, the high-pressure cylinder (Fig. 4) was made from a piece of Nickel Chrome steel, 5 in. in diameter, which was kindly supplied by Messrs Brown Bayley's Steel Works, Ltd., and this was afterwards given by them the necessary heat-treatment.

The hydraulic press was also fitted with screw gear for reversing the  $2\frac{1}{2}$ -inches-diameter piston, and with a needle-valve for letting out the liquid displaced by the piston.

## § 6. THE MEASUREMENT OF THE LONGITUDINAL STRAINS

In the measurement of the longitudinal and diametral strains produced by hydrostatic pressure inside the various cylindrical shells each specimen was held in an upright position and was connected by special steel tubing to the high-pressure apparatus. The scale employed in conjunction with the longitudinal extensometer was placed about 450 centimetres away from the instrument. It was the usual practice to subject the specimen to pressure after having set up the extensometer in position, and then to leave the apparatus for about 30 min. in order to give it time to settle down to a steady temperature.

In taking a set of readings the pressure was applied in equal increments, the value of the increment depending on the dimensions of the cylinder. In most cases the pressure increment was 1.395 tons per sq. in., which corresponded to the addition of 10 lb. to the load platform. At the commencement the scale reading was generally produced by the pressure corresponding to the weight of the load platform itself, but in several experiments at the first reading there was an initial load placed on the platform.

In applying the pressure it was found necessary to work the pump very slowly; by the adoption of this precaution the unknown additional pressure created in overcoming the inertia of the load in its rise, and by friction, was reduced to a minimum. It was also found that the scale reading attained a maximum value and then remained steady for a few seconds, during which interval it was convenient to take the reading corresponding to the load on the floating plunger. Care was of course exercised in the application of the pressure in order to safeguard the cylinder from being overstrained; two specimens were lost by failure to do this.

Table 2: Longitudinal extensions of specimens 7 and 11

SPECIMEN 7.				SPECIMEN 11.			
Outside diam. = 0.8005"				Outside diam. = 0.899"			
Inside diam. = 0.400"				Inside diam. = 0.3995"			
EXTENSOMETER:				EXTENSOMETER:			
$d = 0.06295"$ , $L = 446$ cm., $l = 4.5$ cm.				$d = 0.06265"$ , $L = 398.4$ cm., $l = 5.0$ cm.			
Distance between knife-edges = 2.001"				Distance between knife-edges = 2.007"			
Pressure tons/ inch <sup>2</sup>	Scale reading		Scale differences cm.	Pressure tons/ inch <sup>2</sup>	Scale reading		Scale differences cm.
	No.	cm.			No.	cm.	
1.350	1	11.00	(1) - (6) = 4.47	1.419	1	11.01	(1) - (5) = 2.45
2.745	2	10.11	(2) - (7) = 4.46	2.887	2	11.30	(2) - (6) = 2.46
4.140	3	9.21	(3) - (8) = 4.43	4.355	3	10.68	(3) - (7) = 2.45
5.535	4	8.32	(4) - (9) = 4.42	5.823	4	10.08	(4) - (8) = 2.45
6.930	5	7.43	(5) - (10) = 4.43	7.291	5	9.46	Mean = 2.4525
8.325	6	6.53	Mean = 4.442	8.759	6	8.84	
9.720	7	5.65	Scale difference for pressure increment of 1.395 tons/inch <sup>2</sup> = 0.888 cm.	10.227	7	8.23	Scale difference for pressure increment of 1.468 tons/inch <sup>2</sup> = 0.6131 cm.
11.115	8	4.78		11.695	8	7.63	
12.510	9	3.90					
13.905	10	3.00					

The readings taken in measuring the longitudinal extensions of a cylinder of the 3.48 per cent. nickel steel and of a cylinder of the 0.28 per cent. carbon steel are given in Table 2, in which is also shown the method of arriving at the scale difference for a given pressure increment.

The readings here recorded are representative of those obtained from experiments on the remaining fifteen specimens. It was always possible by careful handling of the pump to obtain a set of scale readings in which the scale differences were constant within one or two per cent. for each equal pressure increment.

A summary of the readings and the results obtained in experiments carried out on the seventeen hollow cylinders are given in Table 3.

Table 3: Summary of results of longitudinal extensional measurements

Specimen	Dimensions of specimens				Extensometer		Longitudinal strains				$\frac{E}{1-2\nu}$ $\div 10^5$	Quality of steel
	Outside diameter inch	Inside diameter inch	$k^2 - 1$	Length inches	Distance between knife-edges inches	$\frac{10^5 d}{4L+2l}$	Pressure increment tons/inch <sup>2</sup>	Scale difference cm.	Strain $\times 10^3$	Strain for pressure 1 ton/inch <sup>2</sup> $\times 10^3$		
1	0.8710	0.5010	2.023	4.0	2.003	3.906	1.468	1.223	2.386	1.626	68.1	Nickel 3.48 %
2	0.8695	0.4995	2.031	5.1	2.000	3.927	1.468	1.243	2.441	1.663	66.3	
3	0.8735	0.5010	2.042	8.1	2.003	3.905	1.468	1.246	2.430	1.655	66.3	
4	0.8743	0.5000	2.056	11.7	2.009	3.875	1.468	1.245	2.402	1.636	66.7	
5	0.6500	0.4995	0.693	5.1	1.998	3.511	0.419	1.150	2.021	4.823	67.0	
6	0.7505	0.5000	1.253	8.1	2.004	3.509	0.698	1.059	1.855	2.657	67.3	
7	0.8005	0.4000	3.004	8.1	2.001	3.510	1.395	0.888	1.558	1.116	66.8	
8	0.7494	0.5005	1.243	4.0	1.997	3.511	0.698	1.030	1.810	2.592	69.5	Carbon 0.28 %
9	0.8755	0.5010	2.054	4.0	1.998	3.509	1.395	1.236	2.171	1.556	70.1	
10	0.7496	0.3760	2.976	4.0	2.000	3.509	1.395	0.860	1.509	1.081	69.6	
11	0.8990	0.3995	4.065	11.6	2.007	3.905	1.468	0.613	1.193	0.813	67.8	
12	0.7502	0.5006	1.247	8.0	2.007	3.511	0.698	1.048	1.833	2.626	68.4	Carbon 0.43 %
13	0.8735	0.5000	2.052	11.6	2.005	3.872	1.468	1.220	2.356	1.605	68.0	
14	0.8000	0.4000	3.000	8.15	1.995	3.506	1.395	0.875	1.541	1.104	67.6	
15	0.9005	0.4000	4.065	11.6	2.000	3.911	1.468	0.610	1.192	0.813	67.8	Carbon 0.09 %
16	0.9363	0.3750	5.234	8.05	2.004	3.509	1.395	0.501	0.877	0.629	68.1	
17	0.7503	0.2495	8.012	8.05	2.003	3.509	2.093	0.492	0.862	0.412	67.8	

If the values of the strain produced by a pressure of one ton per sq. in., in the eleventh column, are plotted against corresponding values of the reciprocal of  $(k^2 - 1)$ , in the fourth column, for specimens 2 to 7 of the 3.48 per cent. nickel steel, and for specimens 11 to 17 of the carbon steels, it is found that each of the two series of points thus plotted lies on a straight line passing through the origin; this shows that the longitudinal strain produced by a given internal pressure applied to various cylinders of the same steel depends inversely on the value of  $(k^2 - 1)$  for the shell.

The figures in the twelfth column of Table 3, under the heading  $E/(1 - 2\nu)$ , were obtained by dividing 2240 by the value of  $(k^2 - 1)$  for the specimen, and by the strain produced by a pressure of one ton per sq. in. It is to be noted how closely

the figures thus calculated agree amongst themselves for specimens 2 to 7, and for specimens 11 to 17, the figures being within 1 per cent. of the mean values  $66.7 \times 10^6$  and  $67.9 \times 10^6$  respectively.

The figures in italics in the twelfth column of Table 3 were obtained from readings taken in experimenting on specimens 1, 8, 9 and 10, all of which were 4 in. long between the screwed ends; and these figures are about 2 per cent. greater than the corresponding values already given.

This question of the effect of the ends of the cylinder on the extension was investigated very carefully in the case of the nickel steel for specimens 1 to 4, all of which had practically the same  $(k^2 - 1)$ , the length of each taken in order being 4, 5.1, 8.1 and 11.7 in. respectively. It would therefore appear from the values given in the twelfth column of Table 3 for these specimens that the ends of the specimen do not influence the longitudinal extensions to any great extent if its length is greater than 5 in. But most of the specimens dealt with were longer than this; in Table 3 it is seen that four were about 11 in. and seven about 8 in. long, the lengths being measured between the screwed ends of the specimens.

As a general rule the agreement between the various sets of readings for a given specimen was very good, but in two or three cases it was observed that in taking a second set of readings immediately after the first set the scale differences were about 2 per cent. greater, though other subsequent sets of readings appeared to agree with the first set within 1 per cent. Having noted this, the author was careful to repeat each experiment several times before removing the specimen from the apparatus.

It should be mentioned here that after the apparatus had been in use for about six months the high-pressure cylinder developed a leak, the result of a flaw in the material, and this necessitated replacing the cylinder by a new one. A new floating plunger was also made together with the fitting in which it works. This explains why in Table 3 the pressure increments are in some cases 1.468 tons per sq. in. and in others 1.395 tons per sq. in. In the former, the pressure is due to the application of a load of 10 lb. on the first plunger of diameter 0.06225 in., while in the latter, the pressure is due to the application of 10 lb. to the second of diameter 0.0638 in.

#### § 7. THE MEASUREMENT OF THE DIAMETRICAL STRAINS

The measurement of the diametral extensions has been done by other investigators with different objects in view. Professors Cook and Robertson carried out in 1910 experiments on "The Strength of Thick Hollow Cylinders under Internal Pressure"\* and Prof. P. W. Bridgman published in 1920 an account of "An Experiment in One-piece Gun Construction."† In both these investigations the measurement of the diametral strains was used chiefly as a means of detecting the pressure at which the material of the thick hollow cylinder yielded. An experiment described by Cook and Robertson in the above paper throws some light on the

\* *Engineering*, 92, 786 (1911).

† *Mining and Metallurgy*, No. 158, Section 14 (1920).

shape of a specimen under internal pressure; it showed that the diametral extensions at various sections are constant near the central portion of the specimen, but near the enlarged ends the extensions are slightly greater. There would thus appear to be some justification for assuming in the case of a long cylindrical shell that each generating line remains straight after the application of the pressure.

The experiments recorded in this section of the present paper were carried out on much the same lines as those already described in the previous section. The specimen was again held in an upright position while under test. The lateral extensometer was placed in contact with the specimen at or near to its middle section, and the instrument was supported lightly by three thin pieces of cord made fast to a plate at the top.

The horizontal scale employed in conjunction with the extensometer was placed about 300 cm. away from the instrument. Since the extensions were much larger in these experiments, it was not necessary to place the scale so far away as in the measurement of the longitudinal extensions.

Table 4: Diametral extensions of specimens 3 and 12.

SPECIMEN 3.				SPECIMEN 12.			
Outside diam. = 0.8735"				Outside diam. = 0.7502"			
Inside diam. = 0.5010"				Inside diam. = 0.5006"			
EXTENSOMETER:				EXTENSOMETER:			
$d = 0.02584", L = 279.5 \text{ cm.}, l = 1.9 \text{ cm.}$				$d = 0.02584", L = 327.2 \text{ cm.}, l = 1.9 \text{ cm.}$			
Pressure tons/ inch <sup>2</sup>	Scale reading		Scale differences cm.	Pressure tons/ inch <sup>2</sup>	Scale reading		Scale differences cm.
	No.	cm.			No.	cm.	
1.350	1	28.11	(1) - (5) = 13.83	2.048	1	24.84	(1) - (6) = 8.26
2.745	2	24.70	(2) - (6) = 13.86	2.467	2	23.20	(2) - (7) = 8.30
4.140	3	21.21	(3) - (7) = 13.81	2.886	3	21.57	(3) - (8) = 8.29
5.535	4	17.80	(4) - (8) = 13.85	3.305	4	19.92	(4) - (9) = 8.37
6.930	5	14.28	Mean = 13.8375	3.724	5	18.26	(5) - (10) = 8.37
8.325	6	10.84		4.143	6	16.58	Mean = 8.318
9.720	7	7.40	Scale difference for pressure increment of 1.395 tons/inch <sup>2</sup> = 3.459 cm.	4.562	7	14.90	
11.115	8	3.95		4.981	8	13.28	Scale difference for pressure increment of 0.419 ton/inch <sup>2</sup> = 1.664 cm.
				5.400	9	11.55	
				5.819	10	9.89	

The readings taken in measuring the diametral extensions of a cylinder of the 3.48 per cent. nickel steel and of a cylinder of the 0.43 per cent. carbon steel are given in Table 4, in which the method of arriving at the scale difference for a given pressure increment is again shown. The readings here recorded are representative of those obtained from experiments on the remaining thirteen specimens. A summary of the readings and the results obtained in experiments carried out on the fifteen specimens is given in Table 5.

If, as in the previous section, the strains produced by a pressure of one ton per sq. in. are plotted against corresponding values of the reciprocal of  $(k^2 - 1)$  for the specimens 2 to 7, and for 11 to 17 respectively, it is found that each of the series of



points lies on a straight line passing through the origin; this shows that the diametral strain produced by a given pressure applied to various cylinders of the same steel depends inversely on the value of  $(k^2 - 1)$  for the shell.

The figures given in the eleventh column of Table 5, under the heading  $E/(2 - \sigma)$ , were obtained by dividing 2240 by the value of  $(k^2 - 1)$  for the specimen and by the diametral strain produced by a pressure of one ton per sq. in. It is to be noted how closely the figures thus calculated agree amongst themselves for specimens 2 to 7 and for specimens 11 to 17. These values are within 1 per cent. of the mean values  $16.81 \times 10^6$  and  $17.22 \times 10^6$  respectively.

Table 5: Summary of results of diametral extensional measurements

Specimen	Dimensions of specimens				Extensometer $\frac{10^3 d}{4L+2l}$	Diametral strains				$\frac{E}{2-\sigma}$ $\div 10^6$	$\frac{e_2}{e_3}$	Quality of steel
	Outside diameter inch	Inside diameter inch	$k^2 - 1$	Length inches		Pressure increment tons/inch <sup>2</sup>	Scale difference cm.	Diametral extension $\times 10^3$ inch	Strain for pressure 1 ton/inch <sup>2</sup> $\times 10^3$			
1	0.8710	0.5010	2.023	4.0	2.305	1.395	3.425	7.894	6.497	17.04	4.00	Nickel 3.48 %
2	0.8695	0.4995	2.031	5.1	2.296	1.395	3.461	7.945	6.549	16.84	3.94	
3	0.8735	0.5010	2.042	8.1	2.305	1.395	3.459	7.971	6.542	16.77	3.95	
5	0.6500	0.4995	0.693	5.1	2.014	0.419	2.605	5.246	19.26	16.78	3.99	
6	0.7505	0.5000	1.253	8.1	1.969	0.419	1.695	3.338	10.61	16.84	3.99	
7	0.8005	0.4000	3.004	8.1	2.230	1.395	2.223	4.958	4.439	16.80	3.98	
8	0.7494	0.5005	1.243	4.0	2.039	0.419	1.582	3.226	10.28	17.54	3.97	Carbor 0.28 %
9	0.8755	0.5010	2.054	4.0	2.251	1.395	3.380	7.607	6.229	17.51	4.00	
0	0.7496	0.3760	2.976	4.0	2.255	1.395	2.010	4.532	4.333	17.37	4.01	
1	0.8990	0.3995	4.065	11.6	2.039	1.395	1.981	4.040	3.221	17.11	3.96	
2	0.7502	0.5006	1.247	8.0	1.969	0.419	1.664	3.275	10.42	17.24	3.97	Carbor 0.43 %
4	0.8000	0.4000	3.000	8.15	2.230	1.395	2.170	4.840	4.336	17.22	3.93	
5	0.9005	0.4000	4.065	11.6	2.041	1.395	1.977	4.034	3.212	17.16	3.95	Carbor 0.09 %
6	0.9363	0.3750	5.234	8.05	1.914	1.395	1.688	3.230	2.474	17.30	3.93	
7	0.7503	0.2495	8.012	8.05	1.730	1.395	0.980	1.694	1.619	17.27	3.93	

The figures in the eleventh column for specimens 1, 8, 9 and 10 are slightly greater than the corresponding mean values just given. But these specimens are the short ones. The ends of the cylinder appear to have only a slight effect on the extensional measurements at the middle section for cylinders 4 in. in length between the screwed ends.

The ratio of the diametral strain  $e_2$  to the longitudinal strain  $e_3$ , both strains being produced by the same internal pressure, is given in the twelfth column of Table 5 for each specimen. Leaving out of consideration the short specimens, it is here seen that this ratio is constant and equal to 3.96 within 1 per cent. for the four varieties of steel dealt with, a result which agrees with equation (8) on page 367.

Let us now see how the result of the investigation fits the usually accepted theory.

Writing  $(2 - \sigma)/(1 - 2\sigma) = 3.96$ , we find that  $\sigma = 0.283$  for the four varieties

of steel. Substituting this in equations (5) and (7), we find that in the case of the nickel steel, since  $E/(1 - \sigma) = 66.7 \times 10^6$ ,  $E = 28.95 \times 10^6$  lb. per sq. in., and since  $E/(2 - \sigma) = 16.81 \times 10^6$ ,  $E = 28.87 \times 10^6$  lb. per sq. in.; also, in the case of carbon steels, since  $E/(1 - \sigma) = 67.9 \times 10^6$ ,  $E = 29.47 \times 10^6$  lb. per sq. in., and since  $E/(2 - \sigma) = 17.22 \times 10^6$ ,  $E = 29.56 \times 10^6$  lb. per sq. in.; and these values of Young's modulus agree fairly well with the usually accepted values for similar steels.

The actual amount of the diametral extension of a cylinder under pressure as given in the ninth column of Table 5 is interesting. In the case of specimen 3, with outside diameter 0.8735 in. a pressure of 13.95 tons per sq. in. increases the diameter by an amount equal to 0.0007971 in., which is less than 0.1 per cent. of the original diameter. Also, in case of specimen 12, with outside diameter 0.7502 in., a pressure of 8.38 tons per sq. in. increases the diameter by an amount equal to 0.000655 in., an amount which is also less than 0.1 per cent. of the original diameter. If the inside diametral extensions of the specimens are of the same order of magnitude there would appear to be some justification for the assumption made in deriving the theory that the alterations in the radial dimensions of the shell are inappreciable after the application of the pressure. The corresponding values of the inside diametral extensions of each of the above cylinders are 0.001145 in. and 0.00085 in. respectively, these being calculated on the assumption that the present theory is correct.

#### § 8. $E$ AND $\sigma$ BY DIRECT TENSION EXPERIMENT

An interesting comparison may be made between these values of  $E$  and  $\sigma$  and those obtained by direct tension of several of the same thick cylinders in a single-lever testing machine employing the same extensometers.

The testing machine could apply loads up to 2 tons, and also loads up to 10 tons could be applied by means of two jockey-weights, the one of weight 168 lb. and the other 672 lb., the two together giving the greater range of load, the smaller alone the lesser range; the beam had two corresponding load scales. The load was applied by a screw operated by worm gearing at the front of the machine. The specimen was secured to the loading gear, and to the beam, by means of an axial loading attachment at both ends, this being held in the grips as shown in Fig. 1.

Before commencing this part of the work a thorough examination of the machine was made. Both jockey-weights were weighed separately, and the weight of each was found to be correct. Then the loading gear was unshipped, and weights up to 0.705 ton were hung from the load shackle of the beam; and in balancing the beam by the smaller jockey-weight it was found that its load scale was correct within the range of load suspended; it was therefore inferred that both the load scales were correct.

The two extensometers were employed in exactly the same manner as has already been described in the previous sections, and they were shielded from the rays of the sun by a large screen.

The effect of the oscillation of the beam of the testing machine on the working of the extensometers was tested and was found to be inappreciable provided the oscillations were not large. Also the effect of a slight tremor, which was always present when the load was being changed, was tested; and this was found to be very slight indeed provided the change of the load was done with care.

The following are the results of experiments carried out on eight of the thick hollow cylinders:

Table 6: Results of tension experiments

Specimen	3	6	7	11	12	14	15	16
$E \div 10^6$	29.8	29.7	29.5	30.5	30.5	30.5	30.4	30.0
Poisson's ratio	0.292	0.293	0.291	0.294	0.291	0.291	0.294	0.290

from which it would appear that for the 3.48 per cent. nickel steel  $E = 29.7 \times 10^6$  lb. per sq. in., and for the carbon steels  $E = 30.4 \times 10^6$  lb. per sq. in., and Poisson's ratio is 0.292 for the four steels. Comparing these with the results of the pressure experiments it is found that

$$(E \text{ by testing machine}) / (E \text{ by pressure experiments}) = 1.027,$$

$$\text{and } (\sigma \text{ by testing machine}) / (\sigma \text{ by pressure experiments}) = 1.032.$$

In view of these discrepancies it was thought advisable to verify the accuracy of the two extensometers.

#### § 9. VERIFICATION OF THE ACCURACY OF THE EXTENSOMETERS

The lateral extensometer had already been checked by Prof. Lamb who mounted the instrument in a measuring machine, and the results of his experiments showed that the extensometer was capable of making a measurement of a lateral extension of 0.0002 in. to within 0.3 per cent.\*

The performance of the 2-in. extensometer was tested against that of three other instruments.

1. Determinations of Young's modulus of four different steel bars by both the 2-in. extensometer and a 4-in. roller extensometer with rollers 0.125 in. diameter were found to be in agreement to within  $\frac{1}{2}$  per cent.

2. Determinations of Young's modulus of a bar of the 3.48 per cent. nickel steel by both the 2-in. instrument and a Ewing's extensometer gave the values  $29.7 \times 10^6$  and  $29.4 \times 10^6$  lb. per sq. in. respectively. But it should be pointed out that the scale difference for a load increment of  $\frac{1}{2}$  ton was about 0.48 in Ewing's extensometer while it was 3.65 in the roller extensometer, the latter being capable of a much finer degree of accuracy.

3. Employing the same bar of nickel steel, Young's modulus was again determined by a 4-in. Marten's extensometer. This gave  $E$  as  $29.4 \times 10^6$  lb. per sq. in.; and in this case for a load increment of  $\frac{1}{2}$  ton the scale difference was about 0.90. For the reason that the exact dimension of the distance across the double knife-

\* *Engineering*, 119, 207 (1925).

edges, when in contact with the surface of the specimen, must always be slightly less than the measured distance, Young's modulus might easily be  $\frac{1}{2}$  per cent. less than the value found by the roller extensometer.

In consideration of these experiments and of the much greater degree of sensitiveness of the roller extensometer compared with either Ewing's or Marten's instruments, one is perhaps justified in regarding the longitudinal extensional measurements of the pressure experiments as being substantially accurate.

If then it is granted that as far as possible experimental errors have been eliminated, and that the theory of the thick cylindrical shell under pressure is correct, the discrepancies in the values of Young's modulus and Poisson's ratio determined by the testing machine and pressure experiments are perhaps due to the non-isotropic nature of the material.

### § 10. CONCLUSIONS

The constants under the heading  $E/(1 - 2\sigma)$  in Table 3 and under the heading  $E/(2 - \sigma)$  in Table 5 are evidently independent of the thickness of the shell, and it may therefore be concluded that they would hold for a thin shell.

On the assumption that the material is non-isotropic, and employing suffixes (2) and (3) for lateral and longitudinal directions respectively, one can write for a thin shell of the nickel steel:

$$1/E_3 - 2\sigma_2/E_2 = 1/66.7 \times 10^6,$$

and

$$2/E_2 - \sigma_3/E_3 = 1/16.81 \times 10^6,$$

from which, making use of the data  $E_3 = 29.7 \times 10^6$  and  $\sigma_3 = 0.292$  as found in the testing machine, we calculate  $E_2$  to be  $28.9 \times 10^6$ , and  $\sigma_2$  to be 0.270. Also, for the three carbon steels, in a similar manner, we calculate  $E_2$  to be  $29.55 \times 10^6$ , and  $\sigma_2$  to be 0.269. Whence the following ratios:

$$E_2/E_3 = 0.973, \text{ and } \sigma_2/\sigma_3 = 0.921.$$

It has been suggested\* that the bulk modulus  $K$  might be obtained from the longitudinal strains of a thick cylindrical shell under internal pressure,  $K$  being equal to  $E/3 (1 - 2\sigma)$ .

From the twelfth column of Table 3, dividing by 3,  $K$  for the nickel steel is  $22.2 \times 10^6$  lb. per sq. in., and for the carbon steels  $22.6 \times 10^6$  lb. per sq. in. Substituting in the formula for  $K$  the values of  $E$  and  $\sigma$  which were obtained in the direct tension experiments on these steels, we obtain that  $K$  is equal to  $23.8 \times 10^6$  and  $24.3 \times 10^6$  respectively, values which are 7 per cent. greater than those already given. But this discrepancy may in a measure be accounted for by slight inaccuracies in the measurements of the longitudinal and lateral strains in determining  $E$  and  $\sigma$  in the testing machine; if, for example, the measured longitudinal strains are  $\frac{1}{2}$  per cent. less, and the lateral strains are 1 per cent. more than the correct amounts, the value of  $K$  as calculated by means of the above formula is about  $2\frac{1}{2}$  per cent. too great. Allowing for this, it would still appear that the

\* A. Mallock, *Trans. Roy. Soc.* (1904); H. Lamb, *Statics*, p. 333.

determination of the bulk modulus by the pressure method yields a low value for this elastic constant.

From the investigations it would appear that when the usually accepted theory is applied in determining the elastic constants of a material, such as steel, by subjecting a thick hollow cylinder to internal pressure, the method, apart from considerations of the difficulty of such experiments, does not give values which are in perfect agreement with those obtained more conveniently in a tensile testing machine.

#### § II. ACKNOWLEDGMENT

The best thanks of the author are due to the Council of the East London College and to Prof. E. H. Lamb for the facilities which have been placed at his disposal for carrying out the work described in this paper.

#### DISCUSSION

Mr J. P. ANDREWS: Mr Wedgwood has attributed the difference between the elastic constants obtained by his pressure method and by the tensile testing machine to anisotropy in his specimens. Since this appears to be of a similar character in all cases, it would probably be due to one or more of the processes required to produce the cylinders employed. Could Mr Wedgwood tell us sufficient about these processes to enable us to gather information as to the effect of working, etc. on the properties of the material? I would like to remark that I have used a lateral extensometer of Prof. Lamb's design, similar to that used by Mr Wedgwood. In my opinion it is amply capable of the accurate measurement of small extensions such as those met with in this investigation. What precautions did Mr Wedgwood take to eliminate the effect of temperature upon this instrument?

Mr SEARS: Mr Wedgwood has described a very good and a very difficult piece of work. The only point which occurred to me to criticise in listening to his paper related to the accuracy of measurement of the pressures employed. I understood him to say that an accuracy of 0.1 per cent. was obtainable, and that he used a plunger  $1/16$ th in. in diameter. To obtain this accuracy of pressure measurement would mean knowing not only the diameter of the plunger, but the mean diameter of the plunger and the hole in which it works, to an accuracy of  $1/32,000$ th in. Even if the plunger were measured to this accuracy it would be very difficult to do the same for the hole. The discrepancy between his values for  $E$  and  $\sigma$  found by pressure measurements in the tensile testing machine is of course much greater than the above amount, but it is possible that the accuracy of pressure measurement might have some bearing on the result.

Dr FERGUSON: Mr Wedgwood's very careful and ingenious experiments show clearly that there is an outstanding discrepancy between the values of Young's modulus and of Poisson's ratio as determined by these two methods. Is it not possible that, under these high pressures, there will be a swelling of the cylinder into a barrel form which is not contemplated by the elementary theory?

MR APPLEYARD: Are the observed differences in  $E$  and  $\sigma$  to be attributed to any measurable extent to differences in the ratio of length to diameter of the specimen tubes?

AUTHOR'S reply: In reply to Mr Andrews: I hardly think that the various processes of the manufacture of the specimens had any effect on the elastic properties of the material of the shells. Had this been the case the discrepancies mentioned would have been greater in the thinner shells. The work of drilling the holes in the longer shells was done very well by the Birmingham Small Arms Company. I consider that the precautions described in the paper were sufficient to eliminate the effects of temperature upon the working of the extensometers.

In reply to Mr Sears: Prof. P. W. Bridgman, who developed the device for measuring the pressures, claimed for it an accuracy of 0.1 per cent. He obtained the "effective area" of the little plunger of his high pressure apparatus hydrostatically by balancing the plunger, which was suitably loaded, against another and larger floating plunger of known diameter. In the present work the diameter of the little plunger was obtained directly by means of a Newall measuring machine, which was capable of making a measurement to the nearest  $2 \times 10^{-5}$  in. The diameter obtained in this way should be correct to within one in three thousand; and if the plunger is a good fit in the hole the measurement of the diameter should be sufficiently accurate for the purpose of this work. The plunger, if one can judge by surface marks, had every appearance of being a good fit when the apparatus was under pressure.

In reply to Dr FERGUSON: Experiments made by Professors Cook and Robertson in 1910 on thick hollow cylinders under internal pressure showed that the diametral extensions are constant near the central portion of the specimen, but near the corners at the enlarged ends the extensions are slightly greater. There would thus appear to be some justification for assuming in developing the theory that each generating line of the cylinder remains straight after the application of the pressure.

In reply to Mr Appleyard: The question of the effects of the ends of the cylinder on the extensions, both longitudinal and diametral, was investigated and I found that in specimens in which the length was about six times the outside diameter the ends did not influence the measured extensions.

# A SIMPLE METHOD OF FITTING A STRAIGHT LINE TO A SERIES OF OBSERVATIONS

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**ABSTRACT.** A method is described for determining the constants in a straight line to represent a series of data. It has a rational basis, and can be carried out in one-third or one-quarter of the time required to apply the method of least squares; it avoids the multiplications and squarings essential to that method, and has the advantage that at no stage does it necessitate the use of more significant figures than are presented in the data to be analysed. The results of the method are compared with those obtained by the method of least squares, on some accurate, and also on some very scattered, observational material. In both cases, the saving of time and labour lead to a negligibly small decrease in accuracy, as compared with the older method.

THE determination of the best linear equation to fit a set of observations is a relatively frequent requirement, since it is involved in all problems of determining the constants in a two-constant equation. For example, the equations  $y = ax^m$ ,  $y = ae^{bx}$  or  $y = ax/(x^2 + b^2)$  reduce to linear equations when written in the forms  $\log y = \log a + m \log x$ ,  $\log y = \log a + bx$ , and  $x/y = x^2/a + b^2/a$ , respectively.

The usual method of dealing with such cases, when the work cannot be conveniently carried out graphically, is to apply the method of least squares, and the object of the present note is to suggest a method which is far less laborious and appears to give results nearly identical with those of the least square method.

In the first place, we may find one point on the line by taking the "centre of gravity" of all the points. That is, if the observations are  $y = y_1, y_2, y_3 \dots y_n$  when  $x$  has the values  $x_1, x_2, x_3 \dots x_n$ , then a point on the line is

$$\bar{y} = \sum_1^n y_r/n, \quad \bar{x} = \sum_1^n x_r/n,$$

where  $n$  is the number of observations. We may note that this point would also be on the line given by the method of least squares, for, taking

$$y = mx + c,$$

as the standard equation to the line, the coefficient of  $c$  in each observational equation is unity, so that the first "normal equation" is

$$\sum_1^n y_r = m \sum_1^n x_r + nc,$$

and the point determined above is clearly consistent with this equation.

We note that the coordinates of this "base-point" need only be determined to the same number of significant figures as the observations themselves.

The next step is to transfer the origin to the base point, by subtracting  $\bar{y}$  and  $\bar{x}$  from each observation, and this reduces the problem to the determination of  $m$  in the equation  $y = mx$ . One method that might suggest itself would be to divide each  $y_r$  in this simple problem by the corresponding  $x_r$ , so as to obtain  $n$  estimates of  $m$ , and to average these; clearly this would not be fair, since the estimate of  $m$  formed as the ratio of two small quantities is entitled to less weight than the estimate from a large  $x_r$  and  $y_r$ . If we weight the estimates according to their values of  $x_r$ , we reproduce the value of  $y_r$ , and thus obtain the very simple rule: To obtain  $m$ , add up all the values of  $x_r$ , and all the values of  $y_r$ , and divide the latter sum by the former.

As regards simplicity, this procedure contrasts strikingly with the method of least squares, which would solve the problem by multiplying every observational equation by  $x_r$  and forming the normal equation

$$\Sigma x_r y_r = m \Sigma x_r^2.$$

The formation of  $2n$  multi-figured products and the addition of the two columns are replaced by the addition of two columns, each consisting of numbers with a smaller number of significant figures.

It is clear that the result cannot differ much from that furnished by the least square method, for in the latter,  $m$  is given as  $\Sigma x_r y_r / \Sigma x_r^2$ . But  $y_r$  is approximately equal to  $m x_r$ , so that the method of least squares gives approximately

$$m = \Sigma m x_r^2 / \Sigma x_r^2,$$

whereas we propose taking

$$m = \Sigma m x_r / \Sigma x_r.$$

When the origin is removed to the centre of gravity of the observations, it is clear that some figures will become negative, others positive. If a line which lies in the first and third quadrants be considered, the estimation of  $m$  for a point in the third quadrant is unaffected by changing the signs of both  $x_r$  and  $y_r$ . If, however, the point is in the second or fourth quadrants, the point tends to rotate the line anti-clockwise, so that only one sign must be changed.

We may sum up the whole procedure as follows, commencing with the table of values of  $x_r$  and  $y_r$ . (1) Sum both columns algebraically, and take the mean of each, viz.  $\bar{x}$  and  $\bar{y}$ . (2) Subtract  $\bar{x}$  from each  $x_r$  and  $\bar{y}$  from each  $y_r$ , to give  $x_r'$  and  $y_r'$ . (3) Make every  $x_r'$  positive, at the same time changing the sign of  $y_r'$  when  $x_r'$  is negative. (4)\* Sum the resulting two columns algebraically, and divide one total by the other. The quotient is the value of  $m$  in the equation

$$y = mx + c,$$

while  $c$  is determined since the point  $(\bar{x}, \bar{y})$  is on the line. At no stage is it necessary to use more significant figures than are used to express the observations, this state of affairs being in marked contrast to the necessities of the least square method.

\* Since the deviations are measured from the centre of gravity, it is clear that the arithmetic could be reduced by using only half the observational material, viz. those for which  $x_r'$  is positive originally.



The method has been tested in several cases, both where the observations are of high accuracy, and also where they are so scattered that the selection of the best line to represent them is a matter of some difficulty. The latter case arises sometimes when a small correction is to be determined by internal analysis of a series of observations. Each pair of observations gives an estimate of the correction, and the estimates may differ by very large fractions of the correction itself, although the divergences are small compared with the quantity to be corrected; nevertheless, it will be desirable to smooth the corrections, and apply them to the experiments separately.

*Example I.* The quantities  $t$  and  $R$  in Table 1 are the measured values of the resistance  $R$  of a coil at the temperatures  $t$ , and it was desired to calculate the constants in the line  $R = at + b$ .

Table 1: Comparison with results obtained by method of least squares

$t$	$R$ (observed)	$R$ calc.		Residuals	
		Least squares	New method	Least squares	New method
14.161	48.9169	48.9178	48.9180	- 9	- 11
14.211	48.9265	48.9269	48.9270	- 4	- 5
14.633	49.0039	49.0035	49.0037	+ 4	+ 2
14.642	49.0055	49.0052	49.0053	+ 3	+ 2
15.825	49.2205	49.2200	49.2201	+ 5	+ 4
15.833	49.2218	49.2215	49.2216	+ 3	+ 2
19.289	49.8496	49.8492	49.8492	+ 4	+ 4
19.292	49.8499	49.8497	49.8497	+ 2	+ 2
19.542	49.8954	49.8951	49.8951	+ 3	+ 3
19.574	49.9014	49.9009	49.9010	+ 5	+ 4
19.612	49.9083	49.9078	49.9079	+ 5	+ 4
20.414	50.0532	50.0535	50.0535	- 3	- 3
20.431	50.0566	50.0566	50.0566	$\pm 0$	$\pm 0$
20.449	50.0596	50.0598	50.0599	- 2	- 3
20.670	50.0997	50.1000	50.1000	- 3	- 3
20.688	50.1029	50.1033	50.1033	- 4	- 4
22.036	50.3483	50.3481	50.3481	+ 2	+ 2
22.062	50.3530	50.3528	50.3528	+ 2	+ 2
24.024	50.7093	50.7091	50.7091	+ 2	+ 2
24.029	50.7102	50.7100	50.7100	+ 2	+ 2
24.060	50.7155	50.7157	50.7156	- 2	- 1
24.079	50.7187	50.7191	50.7191	- 4	- 4
26.136	51.0928	51.0927	51.0926	+ 1	+ 2
26.159	51.0969	51.0969	51.0968	$\pm 0$	+ 1
27.299	51.3041	51.3039	51.3038	+ 2	+ 3
27.300	51.3042	51.3041	51.3040	+ 1	+ 2

The calculation by the method of least squares occupied some three hours, and gave the result  $R = 46.3459 (1 + 0.391879 t)$ . The present method was also applied. It occupied about one hour, and gave the result  $R = 46.3463 (1 + 0.391835 t)$ . The full calculation by the present method is shown in Table 2, whilst the real degree of agreement between the two equations may perhaps be better estimated from the last four columns of Table 1, which give successively the calculated values of  $R$  from the two equations, and the residuals ( $R_{\text{observed}}$  less  $R_{\text{calculated}}$ ), the unit for the residuals being one unit in the fourth decimal place.

Table 2: Example of method of calculation

$t$	$R$	$(t - 20.633)$	$\pm (R - 50.0933)$
14.161	48.9169	6.472	1.1764
14.211	48.9265	6.422	1.1668
14.633	49.0039	6.000	1.0894
14.642	49.0055	5.991	1.0878
15.825	49.2205	4.808	0.8728
15.833	49.2218	4.800	0.8715
19.289	49.8496	1.344	0.2437
19.292	49.8499	1.341	0.2434
19.542	49.8954	1.091	0.1979
19.574	49.9014	1.059	0.1919
19.612	49.9083	1.021	0.1850
20.414	50.0532	0.219	0.0401
20.431	50.0566	0.202	0.0367
20.449	50.0596	0.184	0.0337
20.670	50.0997	0.037	0.0064
20.688	50.1029	0.055	0.0096
22.036	50.3483	1.403	0.2550
22.062	50.3530	1.429	0.2597
24.024	50.7093	3.391	0.6160
24.029	50.7102	3.396	0.6169
24.060	50.7155	3.427	0.6222
24.079	50.7187	3.446	0.6254
26.136	51.0928	5.503	0.9995
26.159	51.0969	5.526	1.0036
27.299	51.3041	6.666	1.2108
27.300	51.3042	6.667	1.2109
Mean $t = 20.633$	Mean $R = 50.0933$	Sum = 81.900	Sum = 14.8731

$$\frac{14.8731}{81.900} = 0.181601.$$

When

$$t = 0, R = 50.0933 - (0.181601 \times 20.633) = 46.3463.$$

Hence linear relation is

$$R = 46.3463 + 0.181601 t = 46.3463 (1 + 0.391835 t).$$

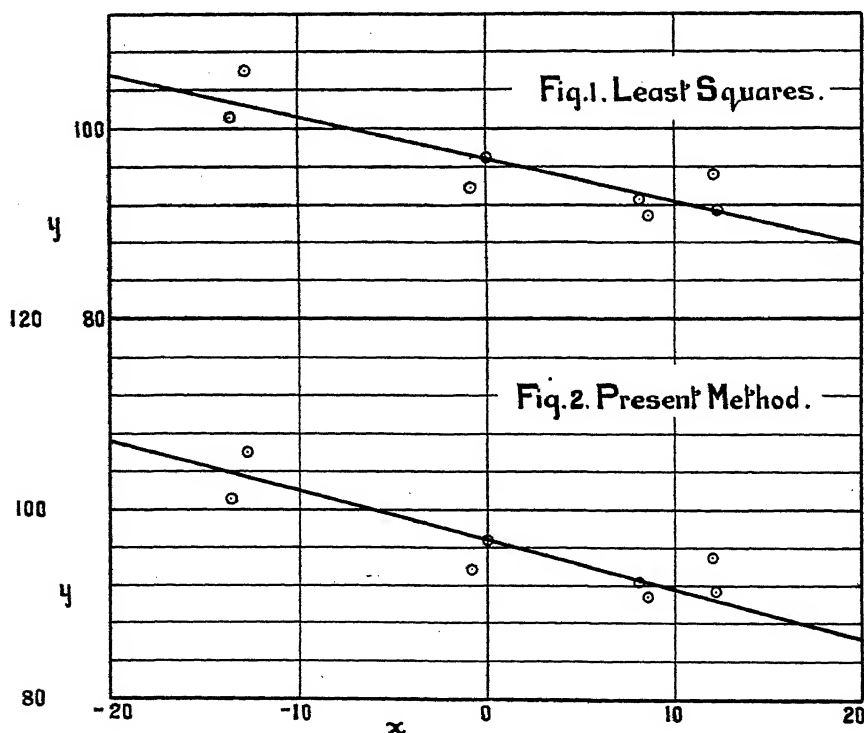
In order to find whether the satisfactory agreement with the least square method was fortuitous in this case, an exactly similar comparison was made with two other series of experimental results. They were actually similar measurements of another resistance coil, and a series of measurements of the two in series. The conclusions may be summarised as follows.

For the measurements quoted above, the mean residual was 0.6, whilst with least squares it was 0.1; meeting the latter method on its chosen ground, the mean square residuals were 12.7 by the new method, and 12.1 by least squares. For the other two series, the present method gave mean residuals of 1.2 and 2.5, as against - 0.5 and - 0.1 by least squares, the mean square residual being 15.6 and 45.7, as against 13.9 and 32.7. These results are quite satisfactory, and in fact the new method gives results, for the present series, which could not really be distinguished from those obtained by least squares. The actual consideration of the constants is also of interest. Extrapolating back to 0° C. the resistances may be compared as follows.

Table 3: Consistency of results

	Resistance		Temperature coefficient of wire	
	Least squares	Present method	Least squares	Present method
1st section	46.4894	46.4897	0.391879	0.391829
2nd section	46.3459	46.3463	0.391879	0.391835
1st section + 2nd section	92.8353	92.8360	—	—
1st section + 2nd section measured together in series 3	92.8359	92.8360	0.391869	0.391835

The individual estimates of  $R_0$  agree with those of the least square method to within 0.0007 ohm =  $2/1000^\circ$  C. approximately, but the sum of the two coils agrees even better with the resistance in series than it does when the method of least squares is used. The coefficients of resistance are in agreement throughout in either method, but the present method gives consistently lower values.



*Example II.* This is an example of the scattered type of observations. Here very high accuracy is clearly unnecessary, and the saving of time may frequently be considered even more worth while than it is with observations of high precision. The points through which it is desired to draw a straight line are shown in the figure, and are set out in Table 4, which also shows the results calculated from the

lines  $y = 96.7 - 0.44_4x$  and  $y = 96.8 - 0.51_4x$ , of which the former results from the method of least squares and the latter from the present method. Even in this case, the mean square deviation is only increased from 5.65 to 6.08 by the use of the less laborious method. (The mean deviations in both methods are 0.1 and -0.1).

Table 4: Data of Example II

$x$	$y$	$y$ (calculated)	
		Least squares	Present method
-13.5 <sub>5</sub>	101.2	102.7	103.8
-12.8	106.0	102.4	103.4
-0.8	93.7	97.1	97.2
0.0	96.8	96.7	96.8
8.1	92.5	93.1	92.6
8.6	90.8	92.9	92.4
12.1	95.0	91.3	90.6
12.2 <sub>5</sub>	91.4	91.3	90.5

It may be of interest to compare the lines given by these methods with the lines drawn "by eye" by two observers. One obtained

$$y = 96.5 - 0.39_8x,$$

and another

$$y = 96.6 - 0.51_8x.$$

Thus these lines differ in slope more than do the two lines given by the arithmetical methods.

On the whole, it appears that when the data are of high accuracy, the line given will be extremely close to that obtained by the method of least squares; when they are of low accuracy, the two methods agree sufficiently well to justify the time saved at the expense of the accuracy, and in general it appears that the method proposed may well replace that of least squares for practically all work where the latter method would now be used. The saving in labour is greater for extensive series than for short ones.

## DISCUSSION

Dr J. S. G. THOMAS said that of the many straight lines that could be drawn through a number of points one could undoubtedly be found by the author's method, but the title of the paper did not indicate what was its peculiarity. Was it the best straight line?

Dr FERGUSON: I assume that Mr Awbery's view is that the lines determined by the least squares method are to be taken as standard lines, and he is simply showing that lines determined by his method are unique, in a sense in which lines determined by the fitting of a stretched thread are not unique, and that they are in good agreement with the "least squares" lines, and may be drawn at the expense of considerably less labour.

Mr J. E. SEARS: The method of least squares is liable to give a misleading estimate of accuracy unless the number of observations involved is very large, and therefore unless this condition is fulfilled the extra labour involved in applying the method of least squares is hardly justified if a simpler alternative method is available which is known to give sufficient accuracy.

Dr W. H. ECCLES: The author has compared the respective approximations obtained by his method and the method of least squares by applying them to a few illustrative examples. It would be useful to attempt some more general comparison. For instance the results obtained by the two methods can be seen by inspection of the coefficients of the normal equations to be closer when the points happen to be scattered parallel to the axis of  $y$  than when parallel to the axis of  $x$ , which suggests that accidental choice of axes affects the merit of the simpler approximation. I hope the author will extend his study in this way so as to indicate to users those distributions of points that favour his method and those that do not.

Dr N. R. CAMPBELL (communicated): Mr Awbery has not told us why he prefers his method to that of zero sum, to which it is so closely similar. (The only difference is that, while the zero sum method divides the observations into two groups equal in number, Mr Awbery's method divides them according as  $x$  is greater or less than  $\bar{x}$ .) For, compared with the method of zero sum, his method has some obvious disadvantages. It is much more laborious, since the zero sum method requires only his first operation and part of his fourth. Also it is not as directly applicable to a linear equation with more than two variables.

The zero sum method was (according to Whittaker and Robinson) invented by Tobias Mayer in 1748 but seems to have been forgotten for over 100 years. I described it, and (in ignorance of Mayer's work) gave it a name, in *Phil. Mag.* 39, 177 (1920), and have discussed it further in *Phil. Mag.* 47, 816 (1924) and in my books *Physics* (Camb. Univ. Press, 1920), chap. 17, and *Measurement and Calculation* (Longmans, 1928), chap. 10. It has recently been used by several physicists other than myself in published work.

The results attained by the two methods, and by least squares, are as follows:

Example 1. Least squares  $R = 46.3459 (1 + 0.00391879 t)$ .

Awbery  $46.3463 (1 + 0.00391835 t)$ .

Zero sum  $46.3464 (1 + 0.00391818 t)$ .

Example 2. Least squares  $y = 96.7 - 0.444 x$ .

Awbery  $96.8 - 0.514 x$ .

Zero sum  $96.6 - 0.411 x$ .

In view of the fact that the residuals have an obvious trend in Example 1, so that the assumed formula is only an approximation, there is nothing to suggest that any one of the methods is here more suitable than any other; all are equally consistent and equally inconsistent with the data.

Finally I should like to protest against Mr Awbery's tacit assumption that the accuracy of a method of adjusting observations is to be judged by its agreement with the least square method, which has so often been shown to be entirely devoid of any theoretical foundation.

AUTHOR's reply: In reply to Dr Thomas, I think Dr Ferguson has perfectly expressed my view. I agree also with Mr Sears, and indeed might go further. The method of least squares can be misleading if the distribution of errors is not "normal," even though the number of observations is large. However, most experimental work does in fact lead to a distribution which is approximately normal (a fact which can only be found out by experiment) so that the "least square" answer is in most cases the standard by which I would prefer to judge other methods.

Regarding the points raised by the President, it is true that the axes chosen affect the line obtained; in this respect the method resembles that of least squares. Thus if the line representing two points  $A$  and  $B$  is determined by the method of least squares, it can be either the line  $AB$ , or its perpendicular bisector, according to the axes selected. It is clear that the closeness of the results obtained by the present method, and by the method of least squares, cannot be accurately compared in all cases; otherwise the least-square line could be deduced from the present one and the method would be a variant of the method of conducting the arithmetical operations of least squares. It may, however, be stated that the present method gives greater weight to the points more remote from the centre of gravity of the points. It will agree closely with the method of least squares either if the points are closely condensed near the centre, or if they are in any case very accurately on a line. The difference will, I think, increase as these conditions are departed from.

In reply to Dr Campbell: I have not dealt with the general comparison of methods. Had I done so, I should have mentioned the method of zero sum, as well as a very convenient method for those who do not insist on entirely arithmetical modes of procedure. I prefer the method I have given, because the assignment of some definite system of "weighting," of which I can see the rationale, appeals to me.

ARC SPECTRA IN THE REGION  $\lambda$  1600–2100

BY E. W. H. SELWYN, B.Sc.

*Communicated by Prof. A. Fowler, F.R.S., March 7, 1929.**Read and discussed May 10, 1929*

**ABSTRACT.** A simple method is described of photographing ordinary arc spectra down to about  $\lambda$  1600, and measures are given of the spectra thus observed between  $\lambda$  1600 and  $\lambda$  2100 of thirteen elements. The measures are believed to be of an accuracy sufficient to make them useful as provisional standards of wave-length. A number of lines hitherto unobserved is recorded and additions have been made to the analysis of the spectra of Mg I, Be I and B I.

**D**URING an investigation by Prof. Fowler of the arc spectrum of silicon (Si I) it became necessary to obtain a spectrum of silicon at least approximating to the arc stage and as complete as was reasonably possible in the region  $\lambda$  1600–2100. The opacity of air effectively limits the spectra of arcs in air to about  $\lambda$  1850, but advantage was taken of the transparency of nitrogen in devising, originally for the above purpose, the following method, by which regular arc spectra down to about  $\lambda$  1600 or a little further may be photographed. It was suggested to the author by Prof. Fowler that it would serve a useful purpose to photograph and measure the spectra of the arcs of a number of elements by this method, and these form the subject of the present communication.

A vacuum grating spectrograph (an early model by Messrs Hilger) was used with a fluorite window sealed over the right-hand slit, so that the spectrograph could be exhausted without disturbing any external arrangements. This arrangement, with normal adjustment, gives the region  $\lambda$  1250–2100 (first order) on a 6 cm. plate. A heavy brass ring with a hole drilled radially into the central aperture and cooled by water circulating around its outer circumference was then fixed to the spectrograph centrally over the window. The arc was arranged to lie as close as possible to the ring and a stream of nitrogen from a cylinder was led into and through the central aperture of the ring as if to blow out the arc. It was found that only a moderate stream of nitrogen was necessary to keep the space between the window and arc relatively transparent, and to blow the dust from the arc away from the window. The nitrogen stream was not rapid enough to cause any inconvenience by blowing out the arc. The spectrograph was exhausted to a pressure of the order of 0.01 mm. of mercury.

It is thought that this method should prove useful for obtaining spectra, due mainly to unionised atoms; for the production of spectra in this region (or at least below  $\lambda$  1800) of arc type has hitherto only been accomplished by very special methods (as in the case of carbon for instance) or by introducing self-inductance into

the circuit of a spark in hydrogen, which much reduces the intensity of the light. The results here given for boron (B I) indicate the possibilities of usefulness of the method. The method is easy to use but suffers from the disadvantage that the photographs are not generally successful below about  $\lambda$  1600; but the fact that lines have occasionally been recorded on the plates down to  $\lambda$  1335 suggests that improvements may be possible which would enable records of arc spectra to be made down to the limit of transparency of fluorite, or possibly, if nitrogen be sufficiently transparent at atmospheric pressure, below that.

Even the short range usefully covered is of interest, however, for two reasons. In the first place, impurity lines due to the elements in the early columns of the periodic table commonly occur in this region; and secondly, the scale on which many previous measures have been based is now under suspicion, and it is a matter of some interest to try and obtain wave-lengths on the true International Ångström scale for this region.

The arcs used were, in general, of the type commonly used in spectroscopy, namely two carbon poles, a small hollow in the lower one carrying a salt of the element whose spectrum was required. Acheson graphite rods were used instead of the ordinary carbons in order to avoid pole impurities. Thus carbon lines were always available as standards for wave-length measurements.

The carbon line, the value for which had previously been accepted as  $1931.027 \text{ \AA}^*$ , was considered, in view of previous experience, of doubtful value as a standard, but it was necessary to use this line, at least in the first reduction of the plates. Fortunately Prof. Fowler had been able to secure measures in the second order of a 10-ft. grating of two silicon lines  $\lambda\lambda$  2058, 2124, by means of which, adopted as standards, the wave-length of this line was measured as  $1930.95 \text{ \AA}$ , and this value was used in the reduction of the plates. Thus the standard lines for reducing the plates were as shown in Table 1.

Table 1. Standard lines

C	C	N	C	C
$\lambda$ 1560.27†	$\lambda$ 1656.27†	$\lambda$ 1742.74‡	$\lambda$ 1751.90§	$\lambda$ 1930.95
1560.66	1657.01	1745.26		
1561.38	1657.37			
	1657.92			
	1658.13			

The uses of these standards only involves the possibility of systematic error in the extrapolation to  $\lambda$  2100, amounting to about  $0.05 \text{ \AA}$ . at that wave-length, owing to error in measurement of  $\lambda$  1930.95. Also, when the plates were reduced in this way, the departure from normality ("errors curve") made necessary a correction

\* Bowen and Ingram, *Phys. Rev.* 28, 444 (1926). There is a strong C I line here, but Bowen considers that this is also the position of a C III line. It seems most probable, however, that it is an arc line showing a shift under vacuum spark conditions.

† Bowen, *Phys. Rev.* 29, 238 (1927).

‡ Bowen and Ingram, *Phys. Rev.* 28, 446 (1926). This pair of nitrogen lines invariably appeared on the plates.

§ Fowler and Selwyn, *Proc. Roy. Soc. A*, 118, 42 (1928).



reaching about  $0.10 \text{ \AA.}$  at  $\lambda 2100$ . The proper reduction of the plates therefore required reliable values for the wave-lengths of at least some lines in the neighbourhood of  $\lambda 2100$ .

The method of reduction of the plates was as follows. All the lines were measured and calculated, assuming  $\lambda\lambda 1656.27, 1930.95$  as standards and linear dispersion throughout the plates, the dispersion, of course, being calculated separately from the measures for each plate. The departure from normality could then be estimated over the region  $\lambda 1600-1900$  with fair accuracy, but up to  $\lambda 2100$  the errors curve was still rather indeterminate, although its general form was sometimes suggested by the errors below  $\lambda 1900$ . In the case of copper such an extrapolation of the errors curve suggested wave-lengths for the lines between  $\lambda 1900$  and  $\lambda 2100$  differing systematically from those given by Eder\* for the copper spark. Such a discrepancy had previously been suggested to exist by Shenstone†, who by his analysis of the spectrum Cu II had been able to calculate the wave-lengths of copper lines in this region. As the probable error in these calculated lines was only  $0.02 \text{ \AA.}$ , use was made of them to complete the errors curve. The result of this work was to confirm the value adopted for the carbon line ( $\lambda 1930.95$ ) and to bring the measurements of the copper lines into conformity with those of Exner and Haschek. Silicon impurity lines provided the means of drawing the errors curve throughout its length for several plates. Except in the cases of strontium and barium, it then became possible by utilising impurity lines to draw errors curves for all plates. The similarity in shape and size of these curves strongly suggests that all measures are on the same scale. There is also, where independent comparison is possible, a general agreement between measures of impurity lines occurring on several plates. The lines are, in effect, measured on Shenstone's calculated copper lines and on Prof. Fowler's silicon lines. Also they show, where comparison is possible, satisfactory agreement with Exner and Haschek's measures. There are grounds therefore for believing that the scale is absolute, and there should be little systematic error in the wave-lengths here given.

Table 2 will reduce Eder's measures to the same scale as is adopted here. It was obtained from a comparison of the different measures on copper, silver, gold and aluminium.

Table 2. Corrections to Eder's measures of Cu lines

$\lambda$		$\lambda$		$\lambda$	
1850	+ 0.08 $\text{\AA.}$	1950	+ 0.12 $\text{\AA.}$	2050	+ 0.08 $\text{\AA.}$
1875	+ 0.08	1975	+ 0.14	2075	+ 0.06
1900	+ 0.08	2000	+ 0.14	2100	+ 0.05
1925	+ 0.10	2025	+ 0.11	2125	+ 0.03

The grating used was of one metre radius and had been ruled at the National Physical Laboratory. Although the dispersion is but  $17.5 \text{ \AA. mm.}$  (in the first order) the definition possible is such that the measurement error on a good line is not likely to be more than  $0.03 \text{ \AA.}$  The resolving power in practice depends only on the slit width and fineness of grain of the plates. It should be possible, theoretically, to

\* *Wien. Ber.* 123, II a, 616 (1914).

† *Phys. Rev.* 29, 380 (1927).

separate two lines 0.06 Å. apart at  $\lambda$  1850—a separation equivalent to one of 0.0035 mm. on the plate and requiring a slit of less than that width. Actually it is a matter of great difficulty to resolve lines 0.20 Å. apart, but pairs of double that separation are usually resolved.

The exposure and development of Schumann plates requires some care if satisfactory results are to be obtained. Without a fair amount of contrast the plates are somewhat difficult to measure, but prolonging development with the object of increasing the contrast often fogs the background and seems to increase the “grain” of the plate. In the ordinary way, the plates were developed with a normal two-solution pyro developer. Occasionally the proportion of accelerator was reduced, but restrainer was not added unless the plate was fogging unduly. In fact it is generally no disadvantage to have some fog present as it ensures that faint lines are developed out. Some of the photographs were taken on fine-grain plates specially prepared by Messrs Hilger; there seems to be a definite advantage in using these plates when the utmost possible resolution is required.

A comparison of the different measures made shows that the accuracy of the wave-lengths here given should be better than 0.05 Å., and it is expected that few lines will be in error by more than this amount.

The following tables give the measures which have been made of the lines of the various spectra. Wave-lengths are given in air down to  $\lambda$  2000 and in vacuum below that wave-length. It has been more usual to change over at  $\lambda$  1850, but the publication of Kayser’s “Schwingungszahlen,” which cease at  $\lambda$  2000, renders the place adopted here more convenient as regards conversion into wave-numbers. A dotted line indicates where the change over from  $\lambda_{\text{air}}$  to  $\lambda_{\text{vac.}}$  takes place. In view of the frequent usefulness of such information, details have been given of the series classifications of the lines where this is known.

In the case of beryllium and magnesium new lines have been observed which extend series already known. The plates of boron show doublets extending the series of which the first members were given by Bowen. The intensity and agreement of these lines with the expected positions seems a satisfactory indication of the correctness of their allocation, but, in view of the probable occurrence of doublet and quartet terms other than the regular terms of the series already classified, it would seem desirable to repeat the observations with greater dispersion and resolving power. There are in the measures, it is thought, indications of combinations involving these extra terms.

The sources of the classifications are given at the foot of each table. The notation in all cases except Au I has been brought into line with that which is now generally adopted. In this system the term is written as a capital letter denoting the type (S, P, D, . . .), with the multiplicity number as a superscript on the left, and the inner quantum number as a subscript on the right. The prefix denotes the orbit (*s, p, d, . . .*) occupied by the “series” electron (or electrons in some cases), the preceding numeral being the principal quantum number of the orbit. When this prefix is undashed it denotes that one electron from the outermost normal orbit is in an excited state, or that the atom is unexcited. If the prefix symbol is dashed then two

or more electrons are in excited states, or an electron has been raised from an orbit deeper than that which is outermost in the unexcited state of the atom; the symbol then adopted is that of the higher of the orbits occupied by the electrons. A table of some of the more important configurations and corresponding terms of B I is given for illustration.

Table 3. Predicted terms of B I

K	L	M	N	O	Electrons outside rare gas shell	Adopted prefix	Terms
I <sub>1</sub>	2 <sub>1</sub> 2 <sub>2</sub>	3 <sub>1</sub> 3 <sub>2</sub> 3 <sub>3</sub>	4 <sub>1</sub> 4 <sub>2</sub> 4 <sub>3</sub> 4 <sub>4</sub>	5 <sub>1</sub> 5 <sub>2</sub> 5 <sub>3</sub>			
2	2 I				2s <sup>2</sup> 2p	2p	<sup>2</sup> P
2	2	I			2s <sup>2</sup> 3s	3s	<sup>2</sup> S
2	2	I			2s <sup>2</sup> 3p	3p	<sup>2</sup> P
2	2	I			2s <sup>2</sup> 3d	3d	<sup>2</sup> D
2	2		I		2s <sup>2</sup> 4s	4s	<sup>2</sup> S
2	2		I		2s <sup>2</sup> 4p	4p	<sup>2</sup> P
2	2		I		2s <sup>2</sup> 4d	4d	<sup>2</sup> D
2	2		I		2s <sup>2</sup> 4f	4f	<sup>2</sup> F
2	2			I	2s <sup>2</sup> 5s	5s	<sup>2</sup> S
2	2			I	2s <sup>2</sup> 5p	5p	<sup>2</sup> P
2	2			I	2s <sup>2</sup> 5d	5d	<sup>2</sup> D
2	I 2				2s 2p <sup>2</sup>	2p'	<sup>2</sup> S <sup>2</sup> P <sup>2</sup> D <sup>4</sup> P
2	I I	I			2s 2p 3s	3s'	<sup>2</sup> P <sup>4</sup> P
2	I I	I			2s 2p 3p	3p'	<sup>2</sup> S <sup>2</sup> P <sup>2</sup> D <sup>4</sup> S <sup>4</sup> P <sup>4</sup> D

Combinations between terms may be regarded as regulated by the prefix symbols according to the familiar rules, i.e. a term with prefix *s* may combine with a term with prefix *p*, a *p* with *s* and *d*, a *d* with *p* and *f*, etc. Strong combinations are also to be expected between terms with dashed prefixes and those with similar undashed prefixes—*d* with *d'*, *p* with *p'*, etc. The structure of the combinations between terms is regulated by the inner quantum selection rules applied to the *j*-numbers of the terms themselves; namely,  $\Delta j = \pm 1$  or 0, with the exception of  $0 \rightarrow 0$ .

The roman numerals following the wave-numbers of the lines in the tables indicate, in the ordinary way, the state of ionisation of the atom to which they are due: I denotes that the atom is neutral; II, that it is once ionised; and III, that it is twice ionised.

The classification of the lines in Table 4 is due to Shenstone\*. The notation has been brought into correspondence with that adopted by Shenstone for Ag II and by McLennan and McLay for Au II, except that the "dashing" or "priming" of certain terms has been omitted as unnecessary; the corresponding prefix for those terms prefixed "b" by Shenstone will be 5s (to correspond with the *d*<sup>3</sup>, *s* configuration of the atom).

The classification of Ag II lines is by Shenstone†. Similar results were arrived at by McLennan and McLay‡. The arc doublet is from Fowler§.

\* *Loc. cit.*† *Trans. Roy. Soc. Can.* 22, III, 1 (1928).† *Phys. Rev.* 31, 317 (1928).§ *Report on Series in Line Spectra*, p. 112.

Table 4. Copper lines

$\lambda$ (Int.)	$\nu$	Classification	$\lambda$ (Int.)	$\nu$	Classification
2126.05 (10)	47020.8		2000.35 (6)	49991.3	II 4s $^3D_3-4p$ $^1F_3$
2122.95 (9)	47089.4	II 4s $^1D_2-4p$ $^1D_2$	1989.85 (3)	50255.0	II 4s $^3D_2-4p$ $^3D_1$
2117.33 (1)	47214.4		1979.97 (4)	50505.8	II 4s $^3D_2-4p$ $^1D_2$
2112.06 (8)	47332.1	II 4s $^1D_2-4p$ $^1P_1$	1970.52 (1)	50748.0	II 4s $^3D_2-4p$ $^1P_1$
2104.80 (7)	47495.3	II 4s $^3D_1-4p$ $^3D_2$	1944.63 (2)	51423.7	II 4s $^3D_3-4p$ $^1D_2$
2098.41 (0)	47639.9		1825.42 (2n)	54781.0	
2087.98 (0)	47877.8		1817.35 (0)	55025.2	
2085.33 (1)	47938.6	II 4s $^3D_3-4p$ $^3F_2$	1774.91 (2n)	56340.9	
2079.43 (4n)	48074.6		1741.63 (1n)	57417.5	
2054.98 (7)	48646.7	II 4s $^3D_2-4p$ $^3D_2$	1725.51 (1n)	57953.9	
2043.80 (6)	48912.7	II 4s $^3D_3-4p$ $^3D_3$	1713.46 (1n)	58361.4	
2037.13 (6)	49072.8	II 4s $^3D_2-4p$ $^1F_3$	1703.84 (0)	58691.0	
2035.86 (6)	49103.4	II 4s $^3D_1-4p$ $^3D_1$	1691.10 (0)	59133.1	
2031.07 (0)	49219.1		1688.80 (00)	59213.6	
2025.49 (4)	49354.7	II 4s $^3D_1-4p$ $^1D_2$	1688.03 (00)	59241.0	
2024.40 (5n)	49381.5		1686.78 (0)	59286.3	
2016.89 (1)	49565.3		1685.52 (0)	59328.9	
2015.61 (1)	49597.8	II 4s $^3D_1-4p$ $^1P_1$	1684.80 (0)	59354.2	
2012.96 (0)	49662.1				

Table 5. Silver lines

$\lambda$ (Int.)	$\nu$	Classification	$\lambda$ (Int.)	$\nu$	Classification
2125.47 (0n)	47033.6	II 5p $^3P_2-5d$ $^3D_3$	2033.93 (2)	49150.0	II 5s $^3D_2-5p$ $^1P_1$
2120.48 (8n)	47144.2	II 5s $^3D_1-5p$ $^1D_2$	2015.96 (2)	49588.2	II 5s $^3D_2-5p$ $^3D_1$
2114.77 (0)	47271.5		2000.72 (3)	49965.2	II 5s $^3D_3-5p$ $^1F_3$
2113.87 (10n)	47291.6	II 5s $^3D_3-5p$ $^3D_3$	1994.35 (3)	50141.7	II 5s $^3D_2-5p$ $^1D_1$
2075.65 (0n)	48162.1	II 5p $^3P_1-5d$ $^1D_2$	1933.51 (1)	51719.4	II 5s $^3D_3-5p$ $^1D_2$
2069.86 (4)	48297.1	I 5s $^3S_1-6p$ $^2P_1$	1709.33 (0)	58502.5	
2061.19 (4)	48500.2	I 5s $^2S_1-6p$ $^2P_2$			

Table 6. Gold lines

$\lambda$ (Int.)	$\nu$	Classification	$\lambda$ (Int.)	$\nu$	Classification
2082.07 (15n)	48013.7	II 6s $^3D_3-6p$ $^3P_2$	1855.54 (4)	53892.7	II 6p $^3P_2-6p$ $^1P_1$
2073.52 (0)	48211.8		1854.71 (0)	53916.8	
2065.92 (2)	48390.8	II 6s $^3D_1-6p$ $^3F_2$	1851.53 (0)	54009.4	II 6p $^3P_2-6d$ $^3P_2$
2044.60 (4)	48893.5		1834.28 (5)	54517.3	
2025.49 (7)	49354.7		1833.14 (5)	54551.2	I 1 $^2D_3-d_{23}$
2021.18 (7)	49455.3	I 1 $^2D_3-b_{23}$	1823.27 (4)	54846.5	II 6s $^3D_1-6p$ $^3P_0$
2014.80 (0)	49610.7		1800.62 (7)	55536.4	II 6s $^3D_2-6p$ $^3D_2$
2012.05 (12n)	49684.5		1793.31 (7)	55762.8	II 6s $^3D_2-6p$ $^3P_1$
2000.83 (12n)	49963.0	II 6s $^3D_3-6p$ $^3F_3$	1783.18 (7)	56079.6	II 6s $^1D_2-6p$ $^1F_3$
1991.94 (10)	50202.3		1775.20 (0)	56331.7	
1984.54 (1)	50389.5		1756.13 (2)	56943.4	II 6s $^1D_2-6p$ $^1D_2$
1978.14 (15)	50552.5		1749.78 (4)	57150.0	II 6s $^3D_2-6p$ $^3D_3$
1965.34 (0n)	50881.8		1740.50 (4)	57454.8	II 6s $^3D_3-6p$ $^3F_4$
1951.97 (7)	51230.3	I 1 $^2S_1-2$ $^2P_2$	1725.91 (2)	57940.4	II 6s $^3D_1-6p$ $^3D_1$
1944.72 (3)	51421.3		1720.03 (1)	58138.5	II 6s $^3D_3-6p$ $^3D_2$
1939.24 (5)	51566.6	I 1 $^2D_3-3$ $^2P_2$	1718.27 (2)	58198.1	
1925.26 (3)	51941.0	II 6p $^3F_3-6d$ $^3G_4$	1716.96 (0)	58242.5	
1921.67 (6)	52038.1	II 6s $^1D_2-6p$ $^1P_1$	1711.47 (0n)	58428.3	
1919.63 (8)	52093.4	I 1 $^2D_3-c_{23}$	1673.60 (3)	59751.4	II 6s $^3D_3-6p$ $^3D_1$
1904.55 (0)	52505.8	II 6p $^3F_3-6d$ $^3D_3$	1670.82 (1)	59850.5	
1879.87 (6)	53195.2	I 1 $^2S_1-2$ $^2P_1$	1665.73 (1)	60033.7	I 1 $^2S_1-3$ $^2P_1$
1872.42 (6)	53406.0		1646.66 (0)	60729.0	I 1 $^2S_1-3$ $^2P_2$
1857.22 (5)	53843.9				

The classification in Table 6 is by McLennan and McLay\*. It has been considered advisable not to change the notation adopted by the authors of the analysis of Au I owing to the inclusion of a number of terms whose relation to the atomic configuration is not clear.

Table 7. Beryllium lines

$\lambda$	(Int.)	$\nu$	Classification	$\lambda$	(Int.)	$\nu$	Classification
*2125.70 (5)		47028.5	I $2p^3P_{210}-5s^3S_1$	1956.97 (1n)		51099.4	I $2p^3P_{210}-8s^3S_1$
*2056.06 (9n)		48621.1	I $2p^3P_{210}-5d^3D_{321}$	*1943.84 (4n)		51444.6	I $2p^3P_{210}-8d^3D_{321}$
2050.45 (2n)		48754.1		1929.47 (1n)		51827.7	I $2p^3P_{210}-9d^3D_{321}$
2043.13 (1n)		48928.7		1919.62 (1n)		52093.3	I $2p^3P_{210}-10d^3D_{321}$
*2032.80 (5)		49177.3	I $2p^3P_{210}-6s^3S_1$	1912.75 (on)		52280.7	I $2p^3P_{210}-11d^3D_{321}$
*1998.11 (7n)		50047.3	I $2p^3P_{210}-6d^3D_{321}$	*1776.28 (6)		56297.4	II $2p^2P_{21}-3s^3S_1$
1985.34 (2)		50369.2	I $2p^3P_{210}-7s^3S_1$	1721.43 (1)		58091.2	? Al.
*1964.79 (6n)		50896.0	I $2p^3P_{210}-7d^3D_{321}$	1661.48 (2)		60187.3	

Classifications of lines marked by an asterisk in Table 7 are by Bowen and Millikan†. The rest of the lines classified by them in Be I are given in Table 8.

Table 8

$\lambda_{\text{air}}$	$\nu$	Classification	$\lambda_{\text{air}}$	$\nu$	Classification
3321.350	30099.60	$2p^3P_2-3s^3S_1$	2494.734	40072.34	$2p^3P_2-3d^3D_{321}$
3321.089	30101.97	$2p^3P_1-3s^3S_1$	2494.589	40074.67	$2p^3P_1-3d^3D_{21}$
3321.016	30102.63	$2p^3P_0-3s^3S_1$	2494.546	40075.36	$2p^3P_0-3d^3D_1$
2650.776	37713.59	$2p^3P_2-2p'^3P_1$	2350.78	42526.0	$2p^3P_{210}-4s^3S_1$
2650.719	37714.54	$2p^3P_1-2p'^3P_0$	2175.04	45961.8	$2p^3P_{210}-4d^3D_{321}$
2650.645	37715.45	$2p^3P_2-2p'^3P_2$			
2650.618	37715.84	$2p^3P_1-2p'^3P_1$			
2650.562	37716.63	$2p^3P_0-2p'^3P_1$			
2650.467	37717.99	$2p^3P_1-2p'^3P_2$			

The following formulae have been computed for the above series:

$$2p^3P_1 - (m+2)s^3S_1 = 53199.8 - \frac{R}{[m + 1.237248 - 0.057234/m]^2} \quad R = 109737 \quad m = 1, 4, 6.$$

$$2p^3P_1 - (m+1)d^3D = 53224.8 - \frac{R}{[m + 0.836383 + 0.104715/m]^2} \quad R = 109737 \quad m = 2, 7, 9.$$

There is no reason therefore for any alteration of the value 53212.86 adopted by Millikan and Bowen† for the term  $2p^3P_0$ . With the use of this value the terms of the Be I spectrum are given by the above observations as follows:

Table 9. Terms of Be I

$2p^3P_0$	53212.86	$3s^3S_1$	23110.22	$3d^3D_{321}$	13137.50
$2p^3P_1$	53212.18	$4s^3S_1$	10685.1	$4d^3D_{321}$	7249.3
$2p^3P_2$	53209.83	$5s^3S_1$	6182.6	$5d^3D_{321}$	4590.0
		$6s^3S_1$	4033.8	$6d^3D_{321}$	3163.8
		$7s^3S_1$	2841.9	$7d^3D_{321}$	2315.1
		$8s^3S_1$	2111.7	$8d^3D_{321}$	1766.5
$2p'^3P_0$	15497.64			$9d^3D_{321}$	1383.4
$2p'^3P_1$	15496.27			$10d^3D_{321}$	1117.8
$2p'^3P_2$	15494.28			$11d^3D_{321}$	930.4

\* Au I, *Proc. Roy. Soc. A*, 112, 95 (1926); Au II, *Trans. Roy. Soc. Can.* 22, III, 103 (1928).

† *Phys. Rev.* 28, 256 (1926).

‡ *Loc. cit.*

The *s*-terms have thus been extended in Table 9 by two and the *d*-terms by three additional members.

Table 10. Magnesium

$\lambda$ (Int.)	$\nu$	Classification	$\lambda$ (Int.)	$\nu$	Classification
2025·86 (15 <i>n</i> )	49346·7	I 3 <i>s</i> <sup>1</sup> S <sub>0</sub> –4 <i>p</i> <sup>1</sup> P <sub>1</sub>	1707·10 (3 <i>n</i> )	58578·9	I 3 <i>s</i> <sup>1</sup> S <sub>0</sub> –7 <i>p</i> <sup>1</sup> P <sub>1</sub>
1827·97 (8 <i>n</i> )	54705·5	I 3 <i>s</i> <sup>1</sup> S <sub>0</sub> –5 <i>p</i> <sup>1</sup> P <sub>1</sub>	1683·51 (1 <i>n</i> )	59399·7	I 3 <i>s</i> <sup>1</sup> S <sub>0</sub> –8 <i>p</i> <sup>1</sup> P <sub>1</sub>
1747·81 (5 <i>n</i> )	57214·5	I 3 <i>s</i> <sup>1</sup> S <sub>0</sub> –6 <i>p</i> <sup>1</sup> P <sub>1</sub>	1668·57 (0 <i>n</i> )	59931·6	I 3 <i>s</i> <sup>1</sup> S <sub>0</sub> –9 <i>p</i> <sup>1</sup> P <sub>1</sub>

The first two lines given in Table 10 are classified by Fowler\*; the remainder have not previously been recorded. The following formula has been computed from the first, second and fifth lines given above. The series is thus represented (with the exception of the first line given in Fowler's *Report*, which is 90 wave-number units out of its calculated position) within about 1 wave-number unit:

$$3s^1S_0 - (m+2)p^1P_1 = 61668 - \frac{R}{[m + 0.941713 + 0.085341/m]^2} \quad R = 109737 \quad m = 1, 2, 3, \dots$$

The limit thus calculated is 4 units lower than that adopted in Fowler's *Report*. With the limit in the *Report* the above observations yield the terms and Rydberg denominators shown in Table 11.

Table 11. Terms of Mg I

Old Notation	New Notation	Term Value	Rydberg Denominator
2P	4 <i>p</i> <sup>1</sup> P <sub>1</sub>	12325·4	2·9838
3P	5 <i>p</i> <sup>1</sup> P <sub>1</sub>	6966·6	3·9689
4P	6 <i>p</i> <sup>1</sup> P <sub>1</sub>	4457·6	4·9616
5P	7 <i>p</i> <sup>1</sup> P <sub>1</sub>	3093·2	5·9563
6P	8 <i>p</i> <sup>1</sup> P <sub>1</sub>	2272·4	6·9492
7P	9 <i>p</i> <sup>1</sup> P <sub>1</sub>	1740·5	7·9403

Table 12. Calcium lines

$\lambda$ (Int.)	$\nu$	Classification	$\lambda$ (Int.)	$\nu$	Classification
2112·77 (10)	47316·2	II 4 <i>p</i> <sup>2</sup> P <sub>2</sub> –5 <i>d</i> <sup>2</sup> D <sub>3/2</sub>	1814·59 (1)	55108·9	II 4 <i>p</i> <sup>2</sup> P <sub>2</sub> –6 <i>d</i> <sup>2</sup> D <sub>3/2</sub>
2103·24 (8)	47530·6	II 4 <i>p</i> <sup>2</sup> P <sub>1</sub> –5 <i>d</i> <sup>2</sup> D <sub>2</sub>	1807·39 (1)	55328·4	II 4 <i>p</i> <sup>2</sup> P <sub>1</sub> –6 <i>d</i> <sup>2</sup> D <sub>2</sub>
1840·07 (8)	54345·8	II 4 <i>d</i> <sup>2</sup> D <sub>3</sub> –4 <i>f</i> <sup>2</sup> F	1651·99 (1)	60533·1	II 4 <i>s</i> <sup>2</sup> S <sub>1</sub> –5 <i>p</i> <sup>2</sup> P <sub>1</sub>
1838·04 (7)	54405·8	II 3 <i>d</i> <sup>2</sup> D <sub>2</sub> –4 <i>f</i> <sup>2</sup> F	1649·87 (1)	60610·8	II 4 <i>s</i> <sup>2</sup> S <sub>1</sub> –5 <i>p</i> <sup>2</sup> P <sub>2</sub>

Table 13. Strontium lines

$\lambda$ (Int.)	$\nu$	Classification	$\lambda$ (Int.)	$\nu$	Classification
2124·48 (4)	47055·5		1778·51 (7)	56226·8	II 4 <i>d</i> <sup>2</sup> D <sub>3</sub> –6 <i>f</i> <sup>2</sup> F
2052·18 (3)	48713·0	II 5 <i>p</i> <sup>2</sup> P <sub>2</sub> –8 <i>s</i> <sup>2</sup> S <sub>1</sub> ?	1769·65 (6)	56508·4	II 4 <i>d</i> <sup>2</sup> D <sub>2</sub> –6 <i>f</i> <sup>2</sup> F
1995·24 (5)	50119·3	II 5 <i>p</i> <sup>2</sup> P <sub>2</sub> –7 <i>d</i> <sup>2</sup> D <sub>3</sub>	1620·35 (1)	61715·1	II 4 <i>d</i> <sup>2</sup> D <sub>3</sub> –7 <i>f</i> <sup>2</sup> F
1964·67 (3)	50899·1	II 5 <i>p</i> <sup>2</sup> P <sub>1</sub> –7 <i>d</i> <sup>2</sup> D <sub>2</sub>	1612·98 (0)	61997·0	II 4 <i>d</i> <sup>2</sup> D <sub>2</sub> –7 <i>f</i> <sup>2</sup> F

\* *Report on Series in Line Spectra*, p. 117.

Table 14. Barium lines

$\lambda$ (Int.)	$\nu$	Classification	$\lambda$ (Int.)	$\nu$	Classification
2052.97 (2)	48695.0	II $6p\ ^3P_2-9d\ ^3D_3$	1904.16 (1)	52516.6	
2024.18 (4)	49386.9		1786.76 (1)	55967.2	
1999.54 (3)	50011.5	II $6p\ ^3P_1-9d\ ^3D_2$	1694.31 (4)	59021.1	
1985.89 (1)	50355.3		1674.39 (1)	59723.2	
1924.77 (5)	51954.3				

The classifications in Tables 12, 13 and 14 are all from Fowler's *Report*\*, except  $4s\ ^2S-5p\ ^2P$  of Ca II which was recognised by Saunders and Russell†. In the case of strontium and barium there may be a small systematic error in the wave-lengths—a correction was made by fitting an errors curve, typical of the other plates measured, to the errors below  $\lambda\ 1930.95$ . The wave-length scale should therefore be correct at  $\lambda\ 1600$ , any systematic error being proportional to the increase in wave-length above  $1600\ \text{\AA}$ .

Table 15. Zinc lines

$\lambda$ (Int.)	$\nu$	Classification	$\lambda$ (Int.)	$\nu$	Classification
2115.04 (2)	47265.5	I $4p\ ^3P_2-4p'\ ^3P_1$ II $4p\ ^3P-4d\ ^3D$ II $4p\ ^3P-4d\ ^3D$ I $4p\ ^3P_1-4p'\ ^3P_0$ I $\begin{cases} 4p\ ^3P_1-4p'\ ^3P_1 \\ 4p\ ^3P_2-4p'\ ^3P_2 \end{cases}$ I $4p\ ^3P_0-4p'\ ^3P_1$ I $4p\ ^3P_1-4p'\ ^3P_2$ II $4p\ ^3P-4d\ ^3D$ II $4p\ ^2S_1-4p\ ^2P$	2025.49 (15)	49354.7	II $4s\ ^2S-4p\ ^2P$
2111.85 (0)	47336.8		2022.05 (1)	49438.9	
2104.39 (7)	47504.6		1972.46 (2)	50698.1	
2102.19 (2)	47554.3		1921.05 (1)	52054.9	
2099.93 (6)	47605.5		1904.82 (2)	52498.4	
2096.89 (5)	47674.4		1898.92 (1)	52661.5	
2087.12 (6n)	47897.5		1868.82 (1)	53509.7	
2079.02 (6)	48084.1		1822.05 (5)	54883.2	
2070.08 (4n)	48291.9		1813.04 (1)	55156.0	
2064.23 (2)	48428.7		1796.68 (2)	55658.2	
2062.01 (10)	48480.9		1726.79 (1)	57910.9	
2060.03 (1n)	48527.4		1682.11 (5)	59449.2	
2053.27 (2)	48687.2		1671.54 (3)	59825.1	
2050.92 (0n)	48742.9				

Classifications of Zn II lines are due to von Salis‡. The fragmentary PP' group is from Grotrian§. The lines marked ? are suggested as completing the group.

Table 16. Cadmium lines

$\lambda$ (Int.)	$\nu$	Classification	$\lambda$ (Int.)	$\nu$	Classification
1820.37 (0)	54933.9		1669.02 (1n)	59915.4	
1669.45 (0n)	59900.0				

Table 17. Mercury lines

$\lambda$ (Int.)	$\nu$	Classification	$\lambda$ (Int.)	$\nu$	Classification
2052.81 (1)	48698.1	I $6p\ ^3P_2-6p'\ ^3P_1$	1849.68 (20R)	54063.4	I $6s\ ^1S_0-6p\ ^1P_1$
2001.99 (2n)	49934.1		1832.74 (1n)	54563.1	I $6p\ ^3P_1-6p'\ ^3P_1$
1972.94 (3)	50685.8	II $6s\ ^2S-6p\ ^2P$	1775.20 (2n)	56331.7	I $6p\ ^3P_0-6p'\ ^3P_1$
1942.28 (5)	51485.9		1649.90 (3)	60609.7	II $6s\ ^2S-6p\ ^2P$
1869.25 (0)	53497.4				

\* Ca II, p. 127; Sr II, p. 132; Ba II, p. 137.

† *Astrophys. Journ.* 62, 5 (1925).‡ *Ann. der Phys.* 76, 145 (1925).§ *Graphische Darstellung der Spectren*, 2, 151 (1928).

The PP' group in Table 17 is again from Grotrian\*, the singlet  $\lambda$  1849.68 from Fowler's *Report*†. It is notable that this measure does not agree so well with the position calculated from the triplet-singlet inter-combinations as the earlier measure by Wolff. The lines of Hg II are as classified by Carroll‡.

Table 18. Boron lines

$\lambda$ (Int.)	$\nu$	Classification	$\lambda$ (Int.)	$\nu$	Classification
*2089.57 (10n)	47841.4	I $2p^2P_2-2p'^2D_3$	1663.07 (2)	60129.8	I $2p^2P_2-5s^2S_1$
*2088.84 (9n)	47858.1	I $2p^2P_1-2p'^2D_2$	1662.62 (1)	60146.0	I $2p^2P_1-5s^2S_1$
*2067.17 (6)	48359.9	{ I $2s^2S_1-2p^2P_1$	*1624.38 (0)	61562.0	} II $2p^2P_{210}-2p'^2P_{210}$
2066.61 (7n)	48373.0	I	*1624.06 (3)	61574.1	
*2065.78 (1)	48392.4	III $2s^2S_1-2p^2P_2$	*1623.61 (1)	61591.2	
*1842.85 (1)	54263.8	II $2p^2P_1-3s^2S_0$	1607.78 (0)	62197.6	I $2p^2P_{21}-5d^2D_{32}$
*1826.52 (9n)	54748.9	I $2p^2P_2-3d^2D_{32}$	1600.91 (1n)	62464.5	
*1825.97 (8n)	54765.4	I $2p^2P_1-3d^2D_2$	1600.28 (on)	62489.1	
1818.41 (6)	54993.1	I $2p^2P_2-4s^2S_1$	1573.44 (2n)	63555.0	I $2p^2P_{21}-6d^2D_{32}$
1817.90 (5)	55008.5	I $2p^2P_1-4s^2S_1$	1566.64 (1n)	63830.9	
1667.42 (3n)	59972.9	I $2p^2P_2-4d^2D_{32}$	1558.93 (on)	64146.6	
1666.99 (2n)	59988.4	I $2p^2P_1-4d^2D_2$			

Boric acid ( $H_2BO_3$ ) was used on carbon poles as the source of the spectrum detailed in Table 18. Classifications of lines marked by an asterisk are by Bowen and Millikan§ and Bowen||.

The first three pairs  $2p^2P_{21}-(m+1)d^2D_{321}$  give the following series formula:

$$\nu = 66911 - \frac{R}{66927 - [m + 0.923463 + 0.160716/m]^2} \quad R = 109737 \quad m = 2, 3, 4, \dots$$

and the  $2p^2P_{21}-(m+2)s^2S_1$  pairs the following (using  $\lambda$  2497.73, 2496.78,  $\nu$  40024, 40040, given in the *Report*, p. 155, as  $2p^2P_{21}-3s^2S_1$ ):

$$\nu = 66796 - \frac{R}{66812 - [m + 1.073754 - 0.049175/m]^2} \quad R = 109737 \quad m = 1, 2, 3, \dots$$

The adoption of 66840 as the value of  $2p^2P_1$  gives the terms of the B I spectrum shown in Table 19.

Table 19. Terms of B I

$2p^2P_1$ 66840	$3s^2S_1$ 26800	$3d^2D_{32}$ 12075
$2p^2P_2$ 66824	$4s^2S_1$ 11831	$4d^2D_{32}$ 6851
$2p'^2D_{32}$ 18983	$5s^2S_1$ 6694	$5d^2D_{32}$ 4359
		$6d^2D_{32}$ 2993

The wave-lengths given in Table 20 were measured by copper lines introduced for the purpose in addition to the carbon lines, and agree very well with those given by Bowen and Ingram¶. The PP' group of Al I (one line being obscured) was given by Bowen and Millikan\*\*. The classification of Al II lines is by Paschen and Sawyer††, and of Al III by Paschen‡‡. The strong diffuse pair,  $\lambda$  1932, 1936, is of some interest

\* *Loc. cit.* † p. 149. ‡ *Phil. Trans. A*, 225, 366 (1926).

§ B II, *Phys. Rev.* 26, 310 (1925); B III, *Proc. Nat. Acad. Amer.* 10, 199 (1924).

|| B I, *Phys. Rev.* 29, 231 (1927).

¶ *Phys. Rev.* 28, p. 444 (1926).

\*\* *Phys. Rev.* 26, 160 (1925).

†† *Ann. der Phys.* 84, 16 (1927).

‡‡ *Ann. der Phys.* 71, 537 (1923).



Table 20. Aluminium lines

$\lambda$ (Int.)	$\nu$	Classification	$\lambda$ (Int.)	$\nu$	Classification
1990.56 (2)	50237.1	II $3p^1P_1-4d^1D_2$	1766.41 (2)	56612.0	I $3p^2P_2-3p^2P_2$
1936.45 (12n)	51640.9		1765.81 (1)	56631.2	II $3p^2P_1-3p^2P_0$
1932.25 (10n)	51753.1		1763.95 (2)	56691.0	II $3p^2P_{21}-3p^2P_{21}$
1862.75 (1)	53684.1	III $3s^2S_1-3p^2P_1$	1762.97 (1n)	56722.5	I $3p^2P_1-3p^2P_2$
1862.42 (1)	53693.6	II $3p^2P_2-4s^2S_1$	1762.03 (0)	56752.7	II $3p^2P_0-3p^2P_1$
1858.10 (1)	53818.4	II $3p^2P_1-4s^2S_1$	1760.13 (1)	56814.0	II $3p^2P_1-3p^2P_2$
1856.01 (0)	53879.0	II $3p^2P_0-4s^2S_1$	1724.99 (3)	57971.4	II $3p^2P_2-3d^3D$
1854.75 (1)	53915.6	II $4s^2S_1-9p^2P_1$	1721.28 (2)	58096.3	II $3p^2P_1-3d^3D$
1769.19 (1)	56523.1	III $3s^2S_1-3p^2P_2$	1719.46 (1)	58157.8	II $3p^2P_0-3d^3D$
1767.77 (2)	56568.5	I $3p^2P_2-3p^2P_1$	1670.76 (4n)	59853.0	II $3p^2S_0-3p^2P_1$
		II $3p^2P_2-3p^2P_1$			

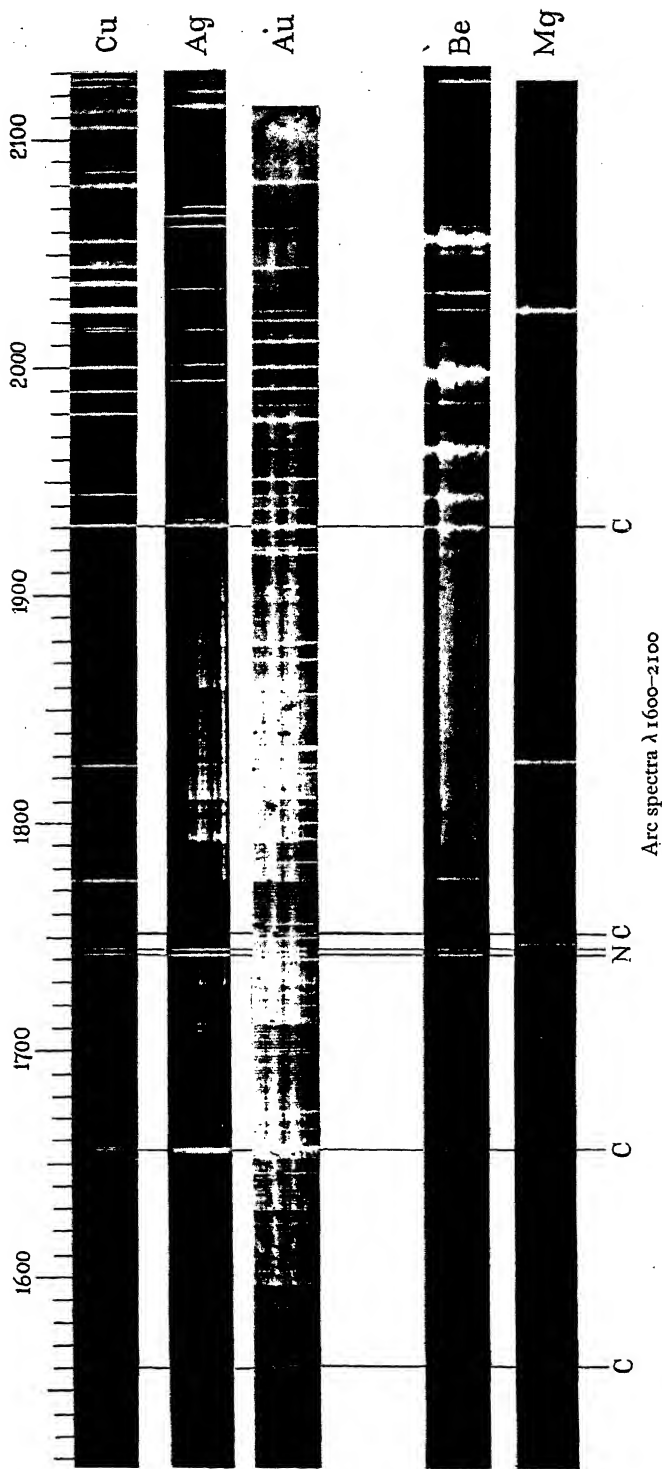
as it has the separation of  $\Delta\nu$  112 of Al I exactly; Paschen and Sawyer allot a number of lines here ( $\lambda\lambda$  1930.03, 1932.43, 1934.54, 1936.96) to a group  $3p^2P'$   $3p''$  of Al II. It seems probable that this pair, which is evidently an arc pair, arises from the combination  $3p^2P_{21}-3p^2S_1$ , the latter term being associated with the electronic configuration  $sp^2$ .

Table 21 is of lines which have appeared as impurities on the plates taken during this investigation. It is thought that this table may be of use in the elimination of impurity lines in spectra in the region concerned. Wave-lengths are given *in vacuo* over the whole range and in air down to  $\lambda$  1800.

Table 21. List of impurity lines

$\lambda_{\text{air}}$	$\lambda_{\text{vac.}}$	Origin	$\lambda_{\text{air}}$	$\lambda_{\text{vac.}}$	Origin
2124.150 (10R)	2124.824	Si I	1935.81 (12n)	1936.45	Al
2089.57 (10n)	2090.24	B I	1931.61 (10n)	1932.25	
2088.84 (9n)	2089.51	"	1900.73 (8R)	1901.36	Si I
2069.86 (4)	2070.52	Ag I	1851.87 (2)	1852.49	"
2062.01 (10)	2062.67	Zn II	1850.08 (4)	1850.70	"
2061.19 (4)	2061.85	Ag I	1847.55 (2)	1848.17	"
2058.139 (5)	2058.801	Si I	1846.86 (3)	1847.48	"
2054.98 (7)	2055.64	Cu II	1844.91 (3)	1845.53	"
2044.60 (4)	2045.26	Au	1840.86 (3)	1841.48	"
2043.80 (6)	2044.46	Cu II	1839.45 (8)	1840.07	Ca II
1037.13 (6)	2037.79	"	1837.42 (7)	1838.04	"
2035.86 (6)	2036.52	"	1827.35 (8n)	1827.97	Mg I
2025.86 (15n)	2026.52	Mg I	1825.90 (9n)	1826.52	B I
2025.49 (15)	2026.15	Zn II	1825.35 (8n)	1825.97	
2024.40 (5n)	2025.05	Cu	1769.19 (1)	1769.19 (1)	Al I
2015.96 (2)	2016.61	Ag II	1766.41 (2)	1766.41 (2)	"
1999.70 (6)	2000.35	Cu II	1765.81 (1)	1765.81 (1)	Al II
1993.70 (3)	1994.35	Ag II	1763.95 (2)	1763.95 (2)	"
1988.36 (6)	1989.01	Si I	1762.97 (1n)	1762.97 (1n)	Al I
1985.74 (4)	1986.39	"	1724.99 (3)	1724.99 (3)	Al II
1982.60 (3)	1983.25	"	1721.28 (2)	1721.28 (2)	"
1978.58 (3)	1979.23	"	1719.46 (1)	1719.46 (1)	"
1976.97 (3)	1977.62	"	1670.76 (4n)	1670.76 (4n)	"
1943.99 (2)	1944.63	Cu II			

I am indebted to Prof. Fowler for permission to use his measures of silicon lines before publication, and I wish to express my appreciation of the help and encouragement I have received from him.









*Note added May 10, 1929.* The investigation of Si I mentioned at the commencement will be found described in *Proc. Roy. Soc. A*, 123, 422 (1929).

## DESCRIPTION OF PLATES

The plates contain reproductions of photographs taken in this investigation; the following details may be of interest.

		Source				Exposure (min.)
Cu	Copper	Metal on carbon poles	...	...	...	10
Ag	Silver	Metal on carbon poles	...	...	...	10
Au	Gold	Metal on carbon poles	...	...	...	15
Be	Beryllium	Metal on carbon poles	...	...	...	10
Mg	Magnesium	Metallic magnesium poles	...	...	...	7
Ca	Calcium	Chloride on carbon poles	...	...	...	10
Sr	Strontium	Chloride on carbon poles	...	...	...	15
Ba	Barium	Hydroxide on carbon poles	...	...	...	20
Zn	Zinc	Metallic zinc and carbon poles	...	...	...	15
Cd	Cadmium	Chloride on carbon poles	...	...	...	20
Hg	Mercury	Mercuric oxide on carbon poles	...	...	...	15
B	Boron	Boric acid on carbon poles	...	...	...	7
Al	Aluminium	Metallic aluminium, copper and carbon poles	...	...	...	10

## DISCUSSION

Dr K. R. RAO: I have used the method described by Mr Selwyn in the course of my investigations on the arc spectra of germanium and arsenic and I wish to record that I have found it peculiarly suitable for the study of arc spectra in the region  $\lambda\lambda$  2000–1560 where it is difficult by the usual methods (e.g. the spark between metallic poles) to differentiate the arc lines from those of the spark.

Mr L. J. FREEMAN: In connection with the appearance of lines down to  $\lambda$  1335, could Mr Selwyn tell us whether the transparency of nitrogen was apparently continuous down to that wave-length?

AUTHOR'S reply: Owing to the formation of oxides of nitrogen by the arc there is some discontinuous absorption over the range for which results are given, and it is possible that this discontinuous absorption continues to regions of shorter wave-length. But nitrogen itself appears to be continuously transparent, or rather, any absorption bands to which it may give rise are comparatively weak and broad. Judging from my own experience, if oxygen could be entirely eliminated from the neighbourhood of the arc, photographs would be secured down to the limit of transparency of fluoride.

# HEAVISIDE'S FRACTIONAL DIFFERENTIATOR

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**ABSTRACT.** Operational methods involve the assumption that the operator may be treated whenever convenient either as an algebraic quantity or as the differentiator of the calculus. They are justified if theorems can be found to cover the processes actually used. Such theorems were simple and often obvious in the early methods of Boole and his immediate successors. In later and more elaborate methods the necessary theorems are usually assumed without proof, so that these methods are only justified by results.

Heaviside fearlessly extended such methods in dealing with the theory of electromagnetic waves. In particular he used fractional powers of  $p$ , though no one has found a meaning for a fractional power of the differentiator  $d/dx$ .

Several important papers have been published, notably those by Bromwich, Jeffreys, and Carson, dealing with Heaviside's work; but it is not unfair to say that they set forth independent parallel methods justifying the results of Heaviside, rather than any explanation of his methods.

In the present paper the operator  $p$  is defined in accordance with Heaviside's rule, but no assumption is made that it is identical with the differentiator of the calculus.

The mathematical functions used in physics consist of series of terms involving powers of the variable  $t$

$$\sum a_n t^n \quad \text{or} \quad \sum c_n \frac{t^n}{n!},$$

where  $a_n$  and  $c_n$  are constants and  $t^n/n!$  is a power term whose index is  $n$ . The operator  $p^\alpha$  is defined simply as an order to reduce by  $\alpha$  the index of each power term to which the operator is applied, thus

$$p^\alpha \sum c_n \frac{t^n}{n!} = \sum c_n \frac{t^{n-\alpha}}{(n-\alpha)!},$$

including

$$p^\alpha \cdot 1 = p^\alpha \frac{t^0}{0!} = \frac{t^{-\alpha}}{(-\alpha)!}.$$

A differential equation  $d^2V/dx^2 = m^2 \cdot dV/dt$  can be regarded as an index relation

$$\frac{d^2V}{dx^2} = m^2 p^1 V \quad \text{or} \quad \left( \frac{d}{dx} - mp^{\frac{1}{2}} \right) \left( \frac{d}{dx} + mp^{\frac{1}{2}} \right) V = 0,$$

by means of which a connection can be found between the co-efficients of a power series in  $t$  assumed for  $V$ . If we can find two power series  $P$  and  $Q$  such that

$$\frac{dP}{dx} = mp^{\frac{1}{2}} P \quad \text{and} \quad \frac{dQ}{dx} = -mp^{\frac{1}{2}} Q,$$

the solution for  $V$  will be

$$V = AP + BQ,$$

where  $A$  and  $B$  are constants.

The power series denoted by

$$P = e^{xmp^{\frac{1}{2}}}, \quad Q = e^{-xmp^{\frac{1}{2}}},$$

or

$$P = 1 + xm \frac{t^{-\frac{1}{2}}}{(-\frac{1}{2})} + \frac{x^2 m^2}{2!} \frac{t^{-1}}{(-1)!} + \text{etc.},$$

with a similar expression for  $Q$ , will fulfil all necessary conditions.

In finding this solution  $p^\alpha$  has been used merely as an index changer without assuming any connection with differentiation.

By proceeding on these lines, and by using Leibnitz's theorem to suggest an operator for fractional powers of  $p$ , it proves possible to establish theorems justifying many of Heaviside's methods.

## § 1. HEAVISIDE'S EXPERIMENTAL METHODS

HEAVISIDE'S mathematical writings are of special interest to the experimental worker in physics. The problems dealt with are of importance in electrical science, and the methods and results have been of great service in electrical technology. Moreover Heaviside's whole outlook upon mathematics was that of an experimenter.

He was "emphatic on the matter of the use of experiment in mathematics even without proper understanding." "It is just the same in mathematical research into unknown regions as in experimental physical research." Theory "can only become logical when the subject is very well known indeed." "Facts and experiments come first."

Fresh work in mathematics, as in other sciences, must be experimental in its early stages. Heaviside held the view that in mathematical research there is a strong tendency to standardise and to become conventional too soon, so that progress is less rapid than might otherwise be the case. No one was ever less willing to follow fashion than Heaviside. He was more interested in devising new methods to get at results quickly than in finding firm proofs of such new methods. He was convinced about results as soon as he could verify them by severe experimental tests, and passed on without waiting to find formal proofs. He was a wanderer in the wilds and loved country far beyond railhead.

A large part of his work on electromagnetic theory relates to the behaviour of waves. His methods involved operators the action of which he interpreted with the aid of his fractional differentiator. This was used merely as a tool in connection with his method, and is to be distinguished from the method itself. He made great use of the tool, but did not profess to explain it, and never regarded the theory of it as one of pressing importance. Criticism of his work has in general referred not so much to his methods as to the use of the fractional operator in conjunction with them, and has been based on the assumption that this operator is identical with the differentiator of the calculus. In what follows I shall try to show that, in order to justify the use of the operator, it is not at all necessary to assume this identity in meaning\*.

## § 2. THE INDEX OPERATOR, ITS DEFINITION AND JUSTIFICATION

Heaviside's fractional differentiator, which is perhaps better described as an index operator, can be defined by the equations

$$p^\alpha t^\beta = \beta! p^\alpha (t^\beta / \beta!) = \beta! [t^{\beta-\alpha} / (\beta - \alpha)!] \quad \dots\dots(1),$$

\* In papers by Bromwich, *Proc. Lond. Math. Soc.* 15, 401-48 (1916), and H. Jeffreys, *Cambridge Tracts in Mathematics*, No. 23, Heaviside's operator is treated on the lines of a complex variable and submitted to contour integration. These papers are of very great interest, but it cannot be claimed that they explain the operator.



where  $t$  is the variable (always real and positive),  $p^\alpha$  the operator, and  $\alpha$  and  $\beta$  are any real quantities. In this definition  $m!$  satisfies the functional equation

$$f(m) = mf(m-1), \quad f(0) = 1 \quad \dots\dots(2),$$

and in order to fix its value definitely between  $0 < m < 1$  Heaviside assumes further that

$$m! = \Gamma(m+1) \quad \dots\dots(3).$$

Now (2) without any aid from (3) makes  $m!$  the product of the first  $m$  natural numbers when  $m$  is a positive integer, and also infinity when  $m$  is a negative integer. Thus whenever  $\alpha$  is a positive or negative integer the operator  $p^\alpha$  has the same effect on a function, as differentiating, or integrating, it  $\alpha$  times. This will be true in (1) whatever  $\beta$  may be. This result however does not identify  $p$  with the differentiator of the calculus.

Heaviside did not arrive at his definition (1) by taking a formula known to be true for integral values of  $\alpha$ , and by assuming it to hold for fractional values. He reached it quite independently from the study of known mathematical solutions of heat diffusion problems\*.

We shall use  $p^\alpha$  merely to specify precisely a change to be made in a power-term, defined as a function of the type  $t^m/m!$ , as a result of which the index  $m$  is altered in accordance with the equation

$$p^\alpha(t^m/m!) = t^{m-\alpha}/(m-\alpha)! \quad \dots\dots(4).$$

This definition involves two points in which we must draw a distinction, even when  $\alpha$  is integral, between  $p$  and the differentiator ( $D \equiv d/dt$ ) of the calculus. These are illustrated by the equations

$$D(at+b) = a, \quad p\left(a \frac{t}{1!} + b \frac{t^0}{0!}\right) = a \frac{t^0}{0!} + b \frac{t^{-1}}{(-1)!}$$

$$D^{-1}a = at + b, \quad p^{-1}\left(a \frac{t^0}{0!}\right) = a \frac{t}{1!} \quad \dots\dots(4a).$$

In the first case  $t^{-1}/(-1)!$  is numerically zero, and we can disregard it in calculation if all the operations are finished; but if we have still to operate upon it by  $p^\alpha$  the quantity really disregarded will be  $t^{-1-\alpha}/(-1-\alpha)!$  and this has a calculable value.

In working with  $p^\alpha$  we must not add a constant on integration, or differentiate a constant away, since by so doing we add or remove a power term. The operator alters but retains each power term, never introduces a new one, and affects nothing but the index of the power term. If the operand  $F$  consists of a group of such terms as

$$F = \sum_s N_s (x^s/s!) \quad \dots\dots(5),$$

the operator simply diminishes by  $\alpha$  the index  $s$  of the power term, without changing  $N_s$ , its numerical coefficient.

\* The fullest statement Heaviside gives of his formula, and an example, almost the only one in his book, showing how he arrived at it, will be found in *Electromagnetic Theory*, 2, 286-90. It should be noted that when he refers to an impulsive quantity as  $p$ , he is using  $p$  in a sense quite distinct from that of his formula, and is thinking of his  $H$  function to which we shall refer at the close of the present paper.

I shall confine this paper to functions each defined, or expansible, as a group of power terms such as (5); and shall merely use such expressions as  $e^x$ ,  $\sinh x$ , etc., as convenient names for such groups. It follows that any equation, or mathematical theorem, denoted by

$$F_1 = F_2 + F_3 + \dots$$

must ultimately be an equation between two groups of power terms and, since this must hold true for any value of the variable, it must really be an identity. By operating throughout by  $p^\alpha$  we merely lower by  $\alpha$  the index of each power term, so that the new equation must also be an identity. This will be the case whatever the relative value of the terms so that no divergency question arises. This fact will be completely disguised by grouping the power terms for convenience in the form of functions with special names, and this disguise may in some cases make the action of  $p^\alpha$  appear mysterious, but does not affect the precise mathematical character of the operation. Any advantage attending the process is a matter for experience, and not for theory, to determine. An ordinary differential equation, even if its coefficients involve the variable, is merely a case of the superposition of such results, and a differential operator involves nothing more whatever the indices used with the operator  $p$ .

This process does not really involve the calculus, and is one of the nature of arithmetic in which we work mechanically to rule without troubling about the theory of the rule. But the process cannot be of use unless two points can be established.

It must be possible, consistently with the assumption about identity of terms, to operate on equations between functions involving infinite series.

It must be possible to establish theorems giving the action of  $p^\alpha$  on combinations of functions like (5) so that results can be obtained with sufficient ease to give the process some advantage in the way of convenience over others.

The first point when examined will be found to involve restraints such as those associated with the divergency of series, or with the remainder term in an ordinary expansion. It proves to be a guide in doubtful cases, and not to offer more difficulty than is found with other methods.

The main point is the second, and here we have the whole of Heaviside's work to assure us that the theorems needed can be established. It is true that Heaviside assumed the theorems without proving them, but he subjected his results to such thorough tests that his work is more convincing than formal proofs sometimes are. It is a direct result of definition (4) that  $p^\alpha$  when applied to any two functions of type (5) gives us

$$p^\alpha (F_1 + F_2) = p^\alpha F_1 + p^\alpha F_2,$$

and that for any two values  $\alpha, \beta$

$$p^{1+\beta} F = p^1 \cdot p^\beta F = p^\beta \cdot p^1 F \quad \dots\dots(6),$$

so that  $p^\alpha$  and  $p^\beta$  are commutative whatever the values of  $\alpha$  and  $\beta$ .

With the help of (4) and (6) some of Heaviside's results can be established without the need of any additional theorem. For consider the differential equation

$$\sigma^2 V = q^2 V \quad \dots\dots(7),$$

where  $\sigma$  is  $d/dx$  and  $q$  a constant. This equation, though obtained by the calculus, can be looked upon simply as a law of indices, and as a matter of fact this is how such equations are often used. The solution of  $(\sigma - q)(\sigma + q)V = 0$  is given as  $AP + BQ$  where  $A$  and  $B$  are constants and  $P$  and  $Q$  satisfy

$$(\sigma - q)P = 0, \quad (\sigma + q)Q = 0 \quad \dots\dots(7a).$$

$P$  and  $Q$  are then assumed to be power series in  $x$  and the equations are used simply as index relations to determine connections between the coefficients of the series, solutions for which are thus proved to be

$$V = \exp(\pm qx).$$

Now if instead of  $q^2$  being constant we have the case

$$\sigma^2 V = m^2 \frac{dV}{dt} \quad \dots\dots(7b),$$

a case which covers many important physical problems, we can use exactly the same argument putting  $q = mp^{\frac{1}{2}}$ . The only difference is that the typical term of the assumed power series instead of being  $q^n x^n/n!$  becomes

$$\frac{m^n x^n}{n!} p^{n/2} = \frac{m^n x^n}{n!} \frac{t^{-n/2}}{(-n/2)!}.$$

We use the facts that  $\sigma$  and  $q$  are independent; that

$$\sigma \cdot \sigma P = \sigma^2 \cdot P,$$

and that

$$p^{\frac{1}{2}} \cdot p^{\frac{1}{2}} P = p \cdot P = dP/dt.$$

We do not in either case use the calculus except in the form of rule (4) and in the latter case we do not assume that  $(d/dt)^{\frac{1}{2}}$  has any meaning, though we do assume, in accordance with (4), that  $p^{\frac{1}{2}}P$  has a definite meaning. The solution

$$V = A \exp(qx) + B \exp(-qx), \text{ where } q = mp^{\frac{1}{2}},$$

as given by Heaviside, has no connection with the exponential theorem; only the two exponential series are involved, and these are as definite functions of  $t$  as of  $x$ , when used, as is assumed, as operators applied to the operand unity, or  $t^0/0!$ . In the above case we can get another solution by assuming for  $P$  and  $Q$

$$P = \sum_{-\infty}^{\infty} \left[ T_n \frac{t^n}{n!} + T_n' \frac{t^{n+\frac{1}{2}}}{(n+\frac{1}{2})!} \right] \quad \dots\dots(7c),$$

with a similar expression for  $Q$ , where  $T_n$  and also  $T_n'$ , are ascending power series in  $x$  with adjustable constants, which can be found, with the aid of the index equations, so as to satisfy all necessary conditions.

We are not concerned with the manipulation involved, or with the choice of a solution to meet the conditions of a particular physical problem. The point is that

Heaviside's method, as put above, seems in this case to make no assumption which was not originally made by Boole in connection with his symbolical methods. When however we take a more complex case\* where

$$q^2 = [r + l(d/dt)] [k + s(d/dt)],$$

and where  $r, l, k, s$  are constants, we find that Heaviside assumed that he could express  $q$ , and any power of  $q$ , in terms of his operator  $p$ , by substituting  $p$  for the differentiator in the above equation and using analysis which is applicable only if  $p$  can be treated as an ordinary variable. The power series in  $p$  so obtained, in this and similar cases, he interpreted by means of (4); he applied the results to physical problems and obtained solutions which in all cases were confirmed when they could be compared with those got by standard methods. Heaviside was however content with overall tests of final results, and did not test intermediate stages. A proof must be such as to make clear and to justify each step. His results have not been challenged, but Heaviside himself never maintained that these results were strictly proved, however confident he was, and had good cause to be, about their correctness. The convenience of his methods has never been disputed. What is needed to complete the proof is the establishment of theorems justifying the steps of his argument. This leads to the consideration of the action of his operator on products, ratios, roots, etc., of functions like (5), and of similar expressions involving the operator itself. In what follows I shall use the Leibnitz theorem to suggest a fractional operator; show that to make the operator work consistently the Heaviside formula must be used; and use the combination, with the aid of the summation formula for the hypergeometric series, to show that consistent results will be got by applying the operator to the two sides of an equation representing a mathematical theorem.

### § 3. THE INDEX OPERATOR AND LEIBNITZ'S THEOREM

Leibnitz's theorem for the successive differentiation of the product of any two functions  $F$  and  $G$  of  $x$  can be regarded as giving the result of the action of an operator determined by  $F$  working on the second function  $G$ . In its original form this operator can be written

$$p^n F = \sum_{n=0}^{\infty} (1/n!) F_n [\alpha! / (\alpha - n)!] p^{\alpha-n} \quad \dots\dots(8)$$

and in its extended form† as

$$\Pi F = \sum_{n=0}^{\infty} 1/n! F_n \Pi_n \quad \dots\dots(8 a),$$

where

$$p \equiv d/dx, \quad F_n \equiv d^n F / dx^n, \quad \Pi_n \equiv d^n \Pi / dp^n,$$

$n$  and  $\alpha$  being each positive integers, and  $\Pi$  a function of  $p$  with powers restricted to integral values.

Let us adopt the right hand element of (8) as the definition of an operator in terms of a standard operator  $p^\alpha$ , where  $\alpha$  may have any value. For convenience we shall call it "the  $hg$  operator" in  $F$ .

\* See (22) below.

† Forsyth, *Differential Equations*, p. 46, 2nd ed. or p. 60, 5th ed.

We propose to consider whether we can so define  $p^\alpha$  that  $p^\alpha$  and  $p^\beta$  are commutative for all real values of  $\alpha$  and  $\beta$ , and are consistent with ordinary differentiations (integrations) when these values are integral .....(9)

$$\text{and} \quad p^\alpha F.G = p^\alpha G.F = p^\alpha.FG \quad \text{.....(10).}$$

Now without defining  $p^\alpha$  let us assume (9) and (10) and take

$$F = x, \quad G = x^m.$$

We shall need to use the relations

$$m! = m(m-1)!, \quad 0! = 1, \quad m! = \Gamma(m+1) \quad \text{.....(11),}$$

$$\text{then if} \quad Z \equiv p^\alpha (x^m/m!) \quad \text{.....(12),}$$

we have by (9) for any integer  $n$

$$p^{\alpha+n} [x^{m+n}/(m+n)!] = p^\alpha.p^n [x^{m+n}/(m+n)!] = p^\alpha (x^m/m!) = Z \quad \text{...(13).}$$

$$\text{Hence} \quad Z = p^{\alpha+1} [x^{m+1}/(m+1)!] = [1/(m+1)!] p^{\alpha+1} x.(x^m/m!),$$

or by (8)

$$(m+1)Z = [xp^{\alpha+1} + (\alpha+1)p^\alpha] (x^m/m!) = (xp + \alpha + 1)Z,$$

thus

$$(m-\alpha)Z = x(dZ/dx),$$

and we have two values for  $Z$  giving

$$p^\alpha (x^m/m!) = x^{m-\alpha}/f(m, \alpha) \quad \text{.....(14),}$$

where  $f(m, \alpha)$  involves  $m$  and  $\alpha$  but not  $x$ . Now if  $\alpha$  is integral we must have whatever  $m$ ,

$$f(m, \alpha) = (m-\alpha)! \quad \text{.....(15),}$$

and this value for  $f(m, \alpha)$  will satisfy a number of functional equations readily obtained from (13), or by applying  $p^{-\alpha}$  to (14), or by putting

$$\alpha = m \pm n,$$

where  $n$  is integral, and operating on  $x^m/m!$  by  $p^\alpha$  or  $p^{\pm n}.p^m$ .

Thus Heaviside's definition

$$p^\alpha (x^m/m!) = x^{m-\alpha}/(m-\alpha)! \quad \text{.....(16),}$$

follows from (14) and (15), satisfies (9) in all cases, and satisfies (10) for the case taken

$$F = x, \quad G = x^m,$$

because from definition

$$p^\alpha.FG = p^\alpha.x^{m+1} = (m+1)! [x^{m+1-\alpha}/(m+1-\alpha)!],$$

and from (8)

$$p^\alpha.F.G = p^\alpha.x.x^m = (xp^\alpha + \alpha p^{\alpha-1})x^m,$$

which reduces to the same result, while

$$p^\alpha.G.F = p^\alpha.x^m.x,$$

like other cases shown below, yields a hypergeometric series which can readily be summed by (17) with the same result as above.

Now assuming definition (16) let us take

$$F = x^3, \quad G = x^\gamma,$$

where  $\beta$  and  $\gamma$  may have any values, and use (8) to test (10). We have

$$p^\alpha F = p^\alpha x^\beta = \sum_{n=0}^{\infty} \frac{1}{n!} \frac{\beta!}{(\beta-n)!} x^{\beta-n} \frac{\alpha!}{(\alpha-n)!} p^{\alpha-n}$$

and

$$p^{\alpha-n} \cdot G = p^{\alpha-n} x^\gamma = \gamma! [x^{\gamma+n-\alpha}/(\gamma+n-\alpha)!].$$

We also have from definition

$$p^\alpha \cdot FG = p^\alpha x^{\beta+\gamma} = (\beta+\gamma)! [x^{\beta+\gamma-\alpha}/(\beta+\gamma-\alpha)!].$$

By substituting in (10) and equating coefficients of  $x^{\beta+\gamma-\alpha}$  we have

$$\frac{(\beta+\gamma)!}{(\beta+\gamma-\alpha)!} = \sum_{n=0}^{\infty} \frac{1}{n!} \frac{\beta!}{(\beta-n)!} \frac{\alpha!}{(\alpha-n)!} \frac{\gamma!}{(\gamma+n-\alpha)!} \dots\dots(17).$$

If we put this in the form

$$\frac{(\beta+\gamma)! (\gamma-\alpha)!}{(\beta+\gamma-\alpha)! \gamma!} = \sum_{n=0}^{\infty} \frac{1}{n!} \frac{\beta!}{(\beta-n)!} \frac{\alpha!}{(\alpha-n)!} \frac{(\gamma-\alpha)!}{(\gamma+n-\alpha)!} \dots\dots(18),$$

we have on the right hand side a hypergeometric series, and on the left, in accordance with the known summation formula, the sum of this series. These facts may be more apparent if we put

$$a + \alpha = -1 = b + \beta,$$

and

$$c = \gamma - \alpha.$$

We then have, after using (11),

$$\alpha! / (\alpha-n)! = (-1)^n [(a+n)! / a!]$$

and a similar expression for  $\beta!$ , etc., so that (18) becomes

$$\frac{(c-a-b-2)! c!}{(c-b-1)! (c-a-1)!} = \sum_{n=0}^{\infty} \frac{1}{n!} \frac{(a+n)! (b+n)! c!}{a! b! (c+n)!}.$$

The ordinary condition for convergence

$$(a+1) + (b+1) < (c+1)$$

becomes in the present notation

$$\beta + \gamma + 1 > 0 \dots\dots(18a),$$

This condition is independent of  $\alpha$ , and only involves the sum of  $\beta$  and  $\gamma$ , which is the index of the power term operated upon. If the series is to be convergent this index must not be  $-1$  or less.

Thus, provided that we use Heaviside's formula in the  $hg$  operator (8) suggested by Leibnitz's theorem, we can use this operator with consistent results in (10) for the product of any two functions of type  $x^\beta$  and  $x^\gamma$ . It follows from simple superposition that this must also be true for any two functions of the general type

$$\sum_s N_s x^s / s!$$

where  $N_s$  is a constant arbitrary for each value of  $s$ . Moreover if

$$F = G_1 \cdot G_2 \dots,$$

where each factor  $G$  is a function of the general type just mentioned, we must get consistent results in working out  $p^\alpha F$  however the factors are operated upon. We can

expand in many ways. We may multiply all the factors and operate on them term by term; or form the  $hg$  operator  $p^a G$ , by taking any factor first, and with the power series in  $p$  so obtained operate on the rest term by term; or use the  $hg$  operator again and so on. But any two series so formed, however complicated they may be, can be shown to have the same sum. No difficulty has been found in proving equality in several most complex cases of this kind.

#### § 4. THE INDEX OPERATOR IN USE WITH BINOMIAL AND EXPONENTIAL EXPANSIONS

The harmonious working of  $p^a$ , the  $hg$  operator, and the binomial theorem, can be shown as follows: let

$$F \equiv \sum_{m=0}^{\infty} \frac{\sigma!}{(\sigma-m)!} \frac{a^m x^m}{m!} = (1+ax)^\sigma \quad \dots\dots(19).$$

If we assume the theorem giving the second expression for  $F$  we are entitled to put

$$F_n = \frac{\sigma!}{(\sigma-n)!} a^n (1+ax)^{\sigma-n} = \frac{\sigma! a^n}{(\sigma-n)!} \sum_{s=0}^{\infty} \frac{(\sigma-n)!}{(\sigma-n-s)!} \frac{a^s x^s}{s!}.$$

Now if we put this in the  $hg$  operator in  $F$  we get

$$p^a F \cdot \frac{x^0}{0!} = \sum_{n=0}^{\infty} \sum_{s=0}^{\infty} \frac{1}{n!} \frac{\sigma!}{(\sigma-n-s)!} \frac{a^{n+s}}{s!} \frac{\alpha!}{(\alpha-n)!} \frac{x^{n+s-\alpha}}{(n-\alpha)!},$$

Now put  $n+s=m$  with limits 0 to  $\infty$  for  $m$ , we get

$$p^a F \cdot 1 = \sum_{m=0}^{\infty} k_m \frac{\sigma!}{(\sigma-m)!} a^m \frac{x^{m-\alpha}}{(m-\alpha)!},$$

where

$$\frac{k_m}{(m-\alpha)!} = \frac{1}{m! 0!} \sum_{n=0}^{\infty} \frac{1}{n!} \frac{m!}{(m-n)!} \frac{\alpha!}{(\alpha-n)!} \frac{0!}{(0+n-\alpha)!},$$

the  $hg$  formula (17) gives  $(m+0)!/(m+0-\alpha)!$  as the sum of this series, so that we find  $k_m = 1$  and we get the same result as by using  $p^a$  on each term of the  $F$  series separately.

Moreover if we expand the  $hg$  operator in  $F$  where  $F$  is the series  $e^{ax}$  so that  $F_n$  is  $a^n e^{ax}$  we get on summing by the binomial theorem the power series\* in  $p$

$$p^a e^{ax} \cdot G = e^{ax} (p+a)^a G \quad \dots\dots(20),$$

where  $G$  is any function of  $x$ ; and from this if  $\Pi(p)$  is any group of power terms in  $p$  it follows from superposition that

$$\Pi(p) e^{ax} \cdot G = e^{ax} \Pi(p+a) G \quad \dots\dots(21),$$

a result also readily following from (8 a) whatever function  $\Pi$  may be of  $p$ , provided we can assume that both the binomial theorem and Taylor's theorem apply, and even without the latter assumption if  $\Pi$  is merely a group of power terms in  $p$ ; indeed the applicability of Taylor's theorem involves the last point. Heaviside made

\* The proof indicated assumes that  $(p+a)^a$  is expanded in fractional powers of  $p$  when  $a$  is fractional. We cannot assume without further investigation that we can use as equivalent the expansion of  $(a+p)^a$  in integral powers of  $p$ .

great use of these theorems in his fractional calculus though he admits that they are only "justified by results." When the powers of  $p$  are integral (20) and (21) are of course well established.

# § 5. FUNCTIONS OF THE OPERATOR

It will be found, on referring to the proof of (19), that, although the convergency of the binomial expansion is assumed, subject to this condition, there is no restriction imposed on the value of  $\sigma$ , which may be negative or fractional. The convergency of the series giving  $k_m$  is assured by the fact that  $m$  is always positive (see (18 a)). It therefore follows from the above that  $p^\alpha$  can be used with consistency on all products, ratios, roots and powers of functions of the variable if reducible to type (5), with or without the use of the binomial theorem; always provided that the corresponding expansions are convergent. We have not dealt with cases of corresponding functions of the differentiator, but the above results encourage the belief, due to Heaviside's work, that theorems can also be established for such cases; a result which will complete the justification of his methods.

This justification is simple enough for cases covered by

$$\sigma^2 F = \Pi F \quad \text{.....(22),}$$

where  $\sigma$  is  $d/dx$  and  $\Pi$  is any quadratic function of  $p$ . Heaviside reduces  $\Pi$  to the form  $(p + \rho)^2 + c$ , and gets rid of  $\rho$  by putting

$$F = G \exp(-\rho t),$$

which reduces the differential equation to the form

$$(\sigma^2 - \Delta^2) G = 0,$$

where  $\Delta^2 = p^2 + c$ . This can be dealt with as in a previous case (7 b) provided we can find, and can justify, an operator  $\Delta$ , which, if applied twice in succession to  $G$ , produces the same result as a single application to it of  $(p^2 + c)$ . The natural expression for  $\Delta$  is  $(p^2 + c)^{\frac{1}{2}}$ , or  $p(1 + c/p^2)^{\frac{1}{2}}$ , but even the meaning of such an expression has to be defined when  $p$  is Heaviside's operator. Now if the binomial expansion of  $(1 + y)^{\frac{1}{2}}$  be denoted by  $B(y)$  we can define  $\Delta$  as  $pB(y)$  where  $y$  is  $c/p^2$ .  $\Delta$  then becomes merely a group of power terms in  $p$  with integral indices, and a perfectly definite meaning attaches to such expressions as  $\Delta G$ ,  $\Delta^2 G$ , etc. All that is needed to justify Heaviside's method is a proof that  $\Delta^2 \equiv p^2 + c$ . Now this results from assuming the binomial theorem for  $pB(y)$ , and for its square; but a more convincing form of proof is obtained by multiplying together the two equal series and collecting terms involving  $y^s$ , or  $(c/p^2)^s$ . We then find

$$\Delta^2 = p^2 \sum_{s=0}^{\infty} K_s \left(\frac{c}{p^2}\right)^s,$$

where  $s! K_s$  is a convergent  $hg$  series taking the form given by (17) where  $\alpha = s$ ,  $\beta = \gamma = \frac{1}{2}$ . This formula thus yields

$$s! K_s = 1/(1 - s)!$$



and, since  $s$  is a positive integer,  $K_s$  vanishes for all values of  $s$  except 0 and 1. We get

$$K_0 = K_1 = 1$$

and

$$\Delta^2 = p^2 \left( 1 + \frac{c}{p^2} \right) = p^2 + c.$$

It is curious that in the general case where  $\Pi$  is a quadratic function of  $p$  the result is reached without using fractional powers of  $p$ ; while in the less general case

$$\Delta^2 = m^2 p$$

fractional powers of  $p$  are involved.

The only inconsistencies, and these but apparent ones, met with in working with  $p^\alpha$ , have been traceable to violation of the formula (4) due to neglect of (4 a) in consequence of the habit of thinking of  $p$  as identical in meaning with the differentiator of the calculus. We must not neglect the existence\* of a power term like  $x^{-m}/(-m)!$  where  $m$  is a positive integer, if it has to be operated upon afterwards by  $p^\alpha$ , where  $\alpha$  is either a fraction or some negative integer equal to or greater than  $m$ . As an instance, let  $F$  be  $e^x$ ,  $\sinh x$ , or  $\cosh x$ . On using the  $hg$  operator we get

$$p^\alpha e^x = (A + B) e^x \quad \dots\dots(23 a),$$

$$p^\alpha \sinh x = A \sinh x + B \cosh x \quad \dots\dots(23 b),$$

$$p^\alpha \cosh x = A \cosh x + B \sinh x \quad \dots\dots(23 c),$$

where  $A$  and  $B$  are each given by

$$\sum_n \frac{1}{n!} \frac{\alpha!}{(\alpha - n)!} \frac{x^{n-\alpha}}{(n - \alpha)!} = \frac{\alpha! \sin \alpha\pi}{\pi} \sum_n \frac{(-1)^n}{n!} \frac{x^{n-\alpha}}{\alpha - n},$$

the values of  $n$  being positive and including all even integers for  $A$  and all odd integers for  $B$ . The second expression is equivalent to the first by a well-known formula. It will be noticed that if  $\alpha$  is integral one of the series reduces to zero and the other to unity, as required.

Now if we differentiate equations (23) in the ordinary way we at first expect that (23 a) will reproduce itself and that (23 b) and (23 c) will interchange. This is not actually the case, except that (23 b) becomes (23 c), since (using the second expression for  $A$  or  $B$ ) we get zero as the value of

$$\sinh x \frac{dA}{dx} + \cosh x \frac{dB}{dx}.$$

This expression with  $A$  and  $B$  interchanged is not zero but a series whose sum can be shown to be

$$-\frac{\alpha! \sin \alpha\pi}{\pi x^{\alpha+1}} = + \frac{x^{-\alpha-1}}{(-\alpha-1)!},$$

and it follows that if we differentiate the right-hand element of (23 a) or (23 c) we get the expected result as increased by this term.

\* When statements are made in print that certain functions of  $p$  (only) are not commutative with each other, the conclusion stated is probably traceable to this cause. For two instances see the top of p. 17 and bottom of p. 18 in Cambridge Mathematical Tract No. 23, *Operational Methods in Mathematical Physics*, by H. Jeffreys.

Now

$$\begin{aligned} p^\alpha p e^x &= p^\alpha \left( e^x + \frac{x^{-1}}{(-1)!} \right), \\ p^\alpha p \sinh x &= p^\alpha \cosh x, \\ p^\alpha p \cosh x &= p^\alpha \left( \sinh x + \frac{x^{-1}}{(-1)!} \right). \end{aligned}$$

So that if we do not dismiss the negative power term we get results quite consistent whichever equation (23) we differentiate.

#### § 6. HEAVISIDE'S OPERATORS

Heaviside's operator as defined in (4) does not seem open to criticism. The striking consistency with which it works in conjunction with mathematical theorems is attributable to special properties of the power term (or index function) due to its association with the gamma function. The most obvious characteristic of the power term is that it appears to retain an existence and individuality of its own whatever operations may be performed upon it. The definition of the index operator  $p^\alpha$  is very simple except that it involves the gamma function whenever  $\alpha$  is fractional (otherwise this function cancels from the equation of definition).

Heaviside's lack of attention to the theory of his operator is striking but characteristic. "It was not the main subject" and he was rarely willing to spend time on side issues. The appeal of his mathematics is due to the fact that he always subordinated it to the problem, arrived at the result required by the shortest route he could find, and used physical conceptions to guide his analysis and prevent it spreading over all the possibilities of a general case. His operator was used as a form of arithmetic with his methods, and these were mostly of his own devising. He would use any known method if convenient, but hardly ever made use of known mathematical results. His method in essence was a mode of getting the formula actually wanted, direct from the differential equation or operator, which he said "not only expresses a problem but also its solution." This should be obtainable from the operator "without ambiguity and without external assistance." He would find a new operator for every fresh type of problem, but would rarely discuss\* it after it had served his purpose.

His methods though 40 years old are not widely known or much used except with periodic forces for which they become much the same as more orthodox ones. They are of most value in cases of incomplete diffusion, and, in particular, in the study of the initial waves due to an impulsive disturbance. We select from his examples in each of these cases one to illustrate the method, and to show that it can be justified without the use of unproved assumptions. Incidentally we shall illustrate the use of his impulse function.

\* One of the most remarkable operators he ever suggested, and one whose great generality appealed to him very strongly, was (*Electromagnetic Theory*, 2, 348) thrown out merely as a side issue. "Incidentally we get this interesting application of physical to pure mathematics... The theorem is very striking. It is obviously true by the method employed, being based upon (103) a simple property; but by pure rigorous mathematics there seems nothing whatever about (it) even suggestive of Bessel functions." He plays with this theorem from the middle of one page to the top of the next, but he does not refer to it again.

## § 7. EXAMPLES

We take first the case of a simplified form of Kelvin's earth cooling problem. If the curvature of the earth's surface be neglected, and  $\theta$  be the temperature at a depth  $x$  beneath the surface, the differential equation covering the problem is

$$d^2\theta/dx^2 = (c/k) d\theta/dt = q^2\theta,$$

where

$$q = \pm (cp/k)^{\frac{1}{2}},$$

$t$  is the time counted from an initial state at which  $\theta$  has the same value  $\theta_0$  for all values of  $x$ , and  $c$ ,  $k$ , and  $g$  are physical constants assumed known,  $g$  being the experimentally measured gradient of temperature at the surface. This is a case covered by (7) and the solution is

$$\begin{aligned}\theta &= \theta_0 e^{-qx}, \\ -\frac{d\theta}{dx} &= q\theta_0 e^{-qx}.\end{aligned}$$

At the surface  $x = 0$  and we have

$$g = q\theta_0 = \left(\frac{c}{k}\right)^{\frac{1}{2}} p^{\frac{1}{2}} \theta_0 = \left(\frac{c}{k}\right)^{\frac{1}{2}} \frac{t^{-\frac{1}{2}}}{(-\frac{1}{2})!} \theta_0.$$

Now  $(-\frac{1}{2})! = \pi$  and Heaviside\* takes

$$k = 0.0118 c, \quad 2743 g = 1, \quad \theta_0 = 4000^\circ \text{C.},$$

whence  $t$  works out to be 103 million years.

We next take the case of a simple one-dimensional problem in which electromagnetic waves travel through the dielectric between the concentric conductors of a cable. The differential equations are

$$-\frac{dV}{dx} = rC + lpC; \text{ and } -\frac{dC}{dx} = kV + spV \quad \dots\dots(24),$$

$V$  and  $C$  being the voltage and current at distance  $x$ , and time  $t$ , while  $r$ ,  $l$ ,  $k$ ,  $s$  are respectively the resistance, inductance, leakage, and capacity, all per unit length of the cable.

If we define  $q$ ,  $\rho$ ,  $\sigma$ , and a velocity  $v$  by the equations

$$\left. \begin{aligned}slv^2 &= 1, & q^2v^2 &= (p + \rho)^2 - \sigma^2 \\ 2\rho &= \frac{r}{l} + \frac{k}{s}, & 2\sigma &= \frac{r}{l} - \frac{k}{s}\end{aligned} \right\} \quad \dots\dots(25),$$

we get from (24)

$$\frac{d^2V}{dx^2} = q^2V, \quad \frac{d^2C}{dx^2} = q^2C \quad \dots\dots(26),$$

and the solutions as justified by (22) above are

$$V = e^{-qx}V_0, \quad C = e^{-qx}C_0 \quad \dots\dots(27),$$

where  $V_0 \equiv F(t)$  is a time function denoting the applied voltage at  $x = 0$ .  $C$  involves both  $x$  and  $t$  but  $C_0$  involves  $t$  only. We suppose the cable to extend indefinitely in

\* *Electromagnetic Theory*, 2, 14.

either direction so that  $x$  may be either  $+$  or  $-$ , but since neither  $V$  nor  $C$  can increase indefinitely with  $x$  the sign chosen for  $q$  in taking the root must be such that  $qx$  is always  $+$ .

Taking first the "distortionless" case with  $\sigma = 0$  or  $r/l = k/s$  we get for positive  $x$

$$qv = p + \rho$$

$$V = \exp \left[ -\frac{x}{v} (p + \rho) \right] F(t) = e^{-p(x/v)} e^{-\rho(x/v)} F(t)$$

$$V = e^{-p(x/v)} F \left( t - \frac{x}{v} \right) \quad \dots\dots(28),$$

and for negative  $x$  we get the same expression with the sign of  $x$  reversed.

Thus we get a positive and a negative wave each moving with velocity  $v$ , without distortion, but attenuating as  $x$  increases in accordance with the factor  $\exp [-(x/v)\rho]$ .

For an ordinary cable  $k$  will be zero but  $\sigma$  will not vanish. The values of  $\rho$  and  $\sigma$  will be the same, but since the attenuation of the wave is determined by the former and the distortion by the latter, we shall retain both symbols in the formulae.

We shall assume that  $V_0$ , which  $\equiv F(t)$ , is constant after  $t = 0$  and zero before.

Since  $k = 0$  we have from (24) and (27)

$$spV = -\frac{dC}{dx} = -\frac{d}{dx} (e^{-qx} C_0) = qC \quad \dots\dots(29),$$

which at  $x = 0$  yields

$$C_0 = s(p/q) V_0 = svV_0(p/qv) \cdot 1.$$

Now using (20) and (21) Heaviside proceeds

$$\frac{p}{qv} \cdot 1 = \frac{p}{\sqrt{(p+\rho)^2 - \sigma^2}} e^{-\rho t} e^{+\rho t} \cdot 1 = e^{-\rho t} \frac{p-\rho}{\sqrt{p^2 - \sigma^2}} e^{\rho t} = e^{-\rho t} \frac{p-\rho}{\sqrt{p^2 - \sigma^2}} \frac{p}{p-\rho} \cdot 1$$

$$= e^{-\rho t} \frac{p}{\sqrt{p^2 - \sigma^2}} \cdot 1 = e^{-\rho t} I(\sigma t) \quad \dots\dots(30),$$

where  $I(\sigma t)$  is defined as the power series in  $t$  resulting from the expansion of

$$p/\sqrt{p^2 - \sigma^2} = [1 - (\sigma^2/p^2)]^{-\frac{1}{2}}$$

in powers of  $(1/p^2)$  transformed afterwards to a function of  $t$  by using Heaviside's formula (4). Now this is the Bessel function satisfying the differential equation

$$(\sigma^2 - p^2) I(\sigma t) = (1/t) p \cdot I(\sigma t) \quad \dots\dots(31).$$

If we change the variable\* from  $t$  to  $T$  where

$$T = t^2$$

\* The proof which follows is more like Heaviside than that which he himself gives (p. 307). This for once follows quite conventional lines, and makes much use of known results. It also shows signs of hurry. Few realise the conditions of publication of Heaviside's *Electromagnetic Theory*. These were most extraordinary for an original work of permanent value. The matter was published week after week and year after year in the *Electrician*. No mathematical author was ever granted so much freedom to publish what, when, and how, he liked, and this freedom was granted by a technical newspaper; but not a line could be changed after first publication, since the type was kept set up till the corresponding section of the book was printed. Reference will show that book and

and use  $P$  for  $d/dT$ , we have

$$p = 2tP \text{ or } 2P = (1/t)p$$

and

$$p^2 = 2P + 2t \frac{dP}{dt} = 2P + 2t^2 \cdot 2P^2 = 2P + 4TP^2 \quad \dots\dots(32),$$

so that (31) becomes

$$(\sigma^2 - p^2) \cdot I(\sigma t) = 2P \cdot I(\sigma T^{\frac{1}{2}}) \quad \dots\dots(33),$$

and this is the value when  $n = 1$  of

$$(\sigma^2 - p^2)^n \cdot I(\sigma t) = \{(2n)!/n!\} P^n \cdot I(\sigma T^{\frac{1}{2}}) \quad \dots\dots(34).$$

So that to establish (34) we have only to prove it true for  $(n + 1)$ , assuming it true for  $n$ , and to do this we have merely to show that

$$(\sigma^2 - p^2) P^n \cdot I(\sigma T^{\frac{1}{2}}) = \{(2n + 2)(2n + 1)/(n + 1)\} P^{n+1} \cdot I(\sigma T^{\frac{1}{2}}),$$

and this can readily be done\*.

If now we refer to (29) and (30) we have

$$\begin{aligned} C/svV_0 &= e^{-qx}C_0/svV_0 = e^{-qx}(p/qv) \cdot 1 = e^{-qx}e^{-\rho t}I(\sigma t) \\ &= e^{-\rho t}e^{-(x/v)\sqrt{p^2-\sigma^2}}I(\sigma t) \quad \dots\dots(35), \end{aligned}$$

where

$$I(\sigma t) = (p/\sqrt{p^2 - \sigma^2}) \cdot 1.$$

On expanding  $\exp[-(x/v)\sqrt{p^2 - \sigma^2}]$  we get a series containing both odd and even powers of  $\sqrt{p^2 - \sigma^2}$ . The former will produce zero when operating on  $I(\sigma t)$ , because, if we substitute for the latter as defined above, we have merely a group of positive integral power terms in  $p$  acting on unity as operand. The even powers will yield integral powers of the operator  $(\sigma^2 - p^2)$  and with the aid of (34) we get a series of the type

$$\sum_{n=0}^{\infty} C_n P^n \cdot I(\sigma T^{\frac{1}{2}}),$$

which on simplification of  $C_n$  will reduce to

$$e^{-(x^2/v^2)P} I(\sigma T^{\frac{1}{2}}) = I\{\sigma[T - (x^2/v^2)]^{\frac{1}{2}}\}.$$

So that we obtain the final result

$$C = svV_0 e^{-\rho t} I\{\sigma[T - (x^2/v^2)]^{\frac{1}{2}}\} \quad \dots\dots(36),$$

and this, as in the two cases represented by (28), consists of two travelling disturbances represented in one case by a positive wave and in the other by a negative

journal correspond word for word. Heaviside never lacked matter, but he must sometimes have wished to deal with a fresh point though under great time pressure. New methods may be shorter and better than old ones, but, even in the hands of their author, they are not always so ready for use. The above seems to be a case in point. A device on the same lines as the simple one here adopted is used by Heaviside himself, and with most striking results, only a few pages later (pp. 327-9). He shows how to separate mathematically the positive from the negative wave, and how to follow each independently.

\* Since  $\sigma^2$  is a number  $\sigma^2 P^n I = P^n \sigma^2 I$ . We can use (33) and (32) to change this expression and also use (32) to change  $p^2 P^n I$ . Finally if we use Leibnitz's theorem to show that

$$P^n 4TP^2 = (4TP^n + 4nP^{n-1})P^2,$$

we obtain the desired relation.

one, each moving with velocity  $v$ , and reaching at any time  $t$  a limiting distance  $vt$ . Of the two time factors, the first represents the attenuation due to  $\rho$ , and the second the combined effect of the distortion due to  $\sigma$  and the translation due to  $v$ .

### § 8. THE IMPULSE FUNCTION

In the above examples, and in other physical problems in which, according to the usual expression, "a force  $F(t)$  is applied at  $t = 0$ ," we can illustrate a use for Heaviside's impulse function. In the physical problem the applied force must always be so stated that it can be calculated for all values of  $t$ , although it is supposed to be non-existent for all negative values of  $t$ . The analysis gives the solution of a more general problem than the one actually stated. Thus, in (28),  $V$  can be calculated not only for negative values of  $t$ , but also for values of  $x$  numerically greater than  $vt$ , though from physical considerations  $V$  cannot exist for such values. A similar remark applies to (36).  $I(z)$  is a power series in  $z$  with only even powers, and thus has a real value even if  $z^2 \equiv \sigma^2 [t^2 - (x^2/v^2)]$  is negative. Heaviside maintained that his operational methods were precise in every respect in regard to the particular problem. He regarded the forces as applied to a physical state in which all the fluxes are originally zero, but adjusted to the initial conditions of the problem by the action of these forces during a short starting interval before the actual commencement of the stated problem. His examples in most cases were concerned with moving electromagnetic waves and with the results of their superposition. He was especially interested in what occurred near the wave front.

He made use of an impulse function of the time which we shall denote by  $H(t)$ . He does not appear to define it precisely but his use of it is consistent with the following statement.

The value  $H$  is either zero or unity except in the close neighbourhood of certain times  $t_1, t_2$ , etc. at which it changes from one of these values to the other. The change is brought about continuously during a short interval of time ( $2c$ ) from  $t - c$  to  $t + c$ , and during this interval it may have any unknown or arbitrarily chosen values consistent with being always real, single-valued and continuous, and with having the right values at the limits. Usually there is only one time  $t = 0$  at which  $H$  changes.  $H = 0$  if  $t \leq -c$ ;  $H = 1$  if  $t \geq +c$ ; and  $H$  is arbitrary if  $-c < t < +c$ .

Now in theory a Fourier series can be found to fulfil these conditions, however small  $c$  may be compared with the unit in terms of which  $t$  is measured.  $H$  is ultimately a power series in  $t$  with positive integral indices. It is real, single-valued and continuous, and can always be differentiated and integrated.

Each applied force given as  $F(t)$  will be associated with a corresponding  $H(t)$  function, such that  $HF$  represents the applied force for all values of  $t$ . The initial conditions can be assumed to result from applying forces such as  $HF$  during the starting interval  $2c$  to a state in which all the fluxes are originally zero. For the problem itself  $t$  is always positive and greater than  $c$ . By Laurent's theorem any  $F(t)$  can be expanded in a power series in  $t$  provided  $t$  is similarly restricted. Finally we can assume  $c$  indefinitely small, and that  $F, H$ , and the product  $FH$  are each power series in  $t$ .

If now we refer to (27) and (28) and use  $HF$  instead of  $F$  for the applied force, we get

$$V = e^{-\rho \cdot x/v} F [t - (x/v)] H [t - (x/v)],$$

a quantity which necessarily vanishes not only when  $t$  is negative, but also when  $x$  exceeds  $vt$ . Similarly in case (29) we must use  $V_0 H$  instead of  $V_0$  and we only arrive at (30) on the assumption that  $H$  is unity, which means that  $t$  must be positive; but even so  $H$  is always a function of  $t$  and as such is present in (30). Equation (34), while true when the operators on the two sides are used as equivalent ones as applied to  $I$ , cannot be assumed true when the operand is  $HI$  unless  $H$  can be assumed to be unity throughout. Each side must vanish if  $t$  is negative, but there appears no obvious way of proving that this is so if  $x$  exceeds  $vt$ . It can however be shown\* that the operator applied to  $HI$  in (35) can be put in the form

$$e^{-\rho t} e^{-(x/v)} (p^2 - \sigma^2)^{\frac{1}{2}} = e^{-\rho t} e^{-(x/v)} p f(1/p),$$

where  $f(1/p)$  only involves negative integral powers of  $p$ .

The operator is thus compounded of three successive operators, one of which attenuates, the next translates, and the third distorts the disturbance denoted by  $HI$ .

The coefficients in the power series  $f(1/p)$  involve  $v$ ,  $x$ , and  $\sigma$  but do not contain the variable  $t$ . We thus have from (35) if  $x$  be positive

$$\begin{aligned} C/svV_0 &= e^{-\rho t} e^{-(x/v)} p f(1/p) H(t) I(\sigma t) \\ &= e^{-\rho t} f(1/p) H[t - (x/v)] I\sigma[t - (x/v)], \end{aligned}$$

which must vanish whenever  $t$  is negative or whenever  $x$  exceeds  $vt$ . If  $x$  be negative a similar relation holds with the sign of  $x$  changed throughout.

The result is not to invalidate (36) but to show that this equation only holds for values of  $t$  and of  $x$  for which

$$t > +c \text{ and } |x| < vt.$$

The above illustration of the use of the impulse function was not actually given by Heaviside, though he possibly regarded it as obvious. It was chiefly in problems involving progressive waves, and the superposition of their effects when they are subjected successively to reflections at boundaries that Heaviside made use of his function. He showed clearly the connection between a moving wave solution and one involving stationary waves as represented by a Fourier series. His work in this connection supplies a physical interpretation of the various formulae which is of great value to anyone interested in physics.

## DISCUSSION

Dr T. J. I'A. BROMWICH (communicated): The statements made by Dr Sumpner (pp. 404, 405) on the general character of Heaviside's methods of working with operational symbols, must be accepted by all students of the subject: but I venture to question the first footnote (on p. 405), with reference to the use of complex integrals as a means of interpreting Heaviside's operators. Speaking for myself, I

\* See *Electromagnetic Theory*, 2, 316-21 (1899). In fact we have  $\log f = (x/v)p \{1 - [1 - (\sigma^2/p^2)]^{\frac{1}{2}}\}$ , which shows that  $\log f$ , and therefore also  $f$  itself, consists of a power series in  $1/p$ .

certainly *do* claim that this interpretation explains the success of Heaviside's work in general: and further that the complex integrals throw light on some points not easily explained in any other way.

Of course no one would suggest that Heaviside himself used complex integrals as an aid to his own discoveries: but his very phrases quoted by Dr Sumpner, seem to indicate that he would have been the last to tie down subsequent workers by insisting on the exclusive use of his own methods. I would add that we were in correspondence on this subject at intervals for some years, starting in 1914; and that he appeared glad to know that a foundation of pure mathematics had been worked out, so as to provide firm footing for the bold and experimental methods of the adventurous pioneer.

Further, the success of Heaviside's methods was due, in a large measure, to his extraordinary power or instinct for detecting hidden sources of error, which might easily lead to unsound conclusions: whereas, if the operators are interpreted in the form of complex integrals, the slippery places reveal themselves to almost any worker with a competent knowledge of modern analysis.

I proceed to illustrate these remarks by some examples; it will be convenient to state at once, without proof, that the complex integral which interprets an operator  $f(p)$  is\*

$$\int_{c-i\infty}^{c+i\infty} \frac{d\lambda}{2\pi i \lambda} f(\lambda) e^{\lambda t},$$

where  $c > 0$ .

It is then fairly easy to prove that if  $f(p)$  is an algebraic function, and is expanded in descending powers of  $p$ , the derived series, which will be in ascending powers of  $t$ , will be convergent, however large  $t$  may be. On the other hand, it is usually found in numerical work, that a definite time-interval  $\tau$  exists, such that when  $t/\tau > 10$ , say, the convergence of the series becomes intolerably slow; so that other means of calculation become essential. Heaviside then expands  $f(p)$  in ascending powers of  $p$ ; and the derived series will proceed in powers of  $\tau/t$  but will not converge. Such series can be proved, from the integral formulae, to have an asymptotic character†, so that the error in stopping at any stage is of the same order as the following term or less.

*Ex. 1. (Electromagnetic Theory, 2, § 242.) Coil at the end of a cable.*

Here  $f(p)$  is of the form  $1/(1 + \sqrt{\tau p})$ : the series

$$\frac{1}{(\tau p)^{\frac{1}{2}}} - \frac{1}{\tau p} + \frac{1}{(\tau p)^{\frac{3}{2}}} - \frac{1}{(\tau p)^2} +$$

leads to the (always convergent) series

$$2 \sqrt{\left(\frac{t}{\pi \tau}\right)} \left\{ 1 + \frac{2}{3} \frac{t}{\tau} + \frac{2 \cdot 2}{3 \cdot 5} \left(\frac{t}{\tau}\right)^2 + \frac{2 \cdot 2 \cdot 2}{3 \cdot 5 \cdot 7} \left(\frac{t}{\tau}\right)^3 + \dots \right\} - (e^{t/\tau} - 1).$$

\* When  $f(p)$  contains fractional powers of  $p$ , the corresponding terms in  $\lambda$  are made one-valued by supposing a cut along the negative part of the real axis: and such powers are positive (and real) on the positive part of the real axis, in the  $\lambda$ -figure. Also the path of integration passes on the positive side (the right-hand, in the usual diagram) of  $\lambda=0$ . See *Proc. Lond. Math. Soc.* (2) 15, 401, §§ 4, 5 (1916); and *Proc. Camb. Phil. Soc.* 20, 411, § 4 (1921).

† A proof is given, for one type, at the end of the second paper just quoted: the reader will have no difficulty in carrying out a similar investigation in other problems.



And the alternative form

$$1 - (\tau p)^{\frac{1}{2}} + (\tau p) - (\tau p)^{\frac{3}{2}} + (\tau p)^2 \dots$$

gives the non-convergent asymptotic series

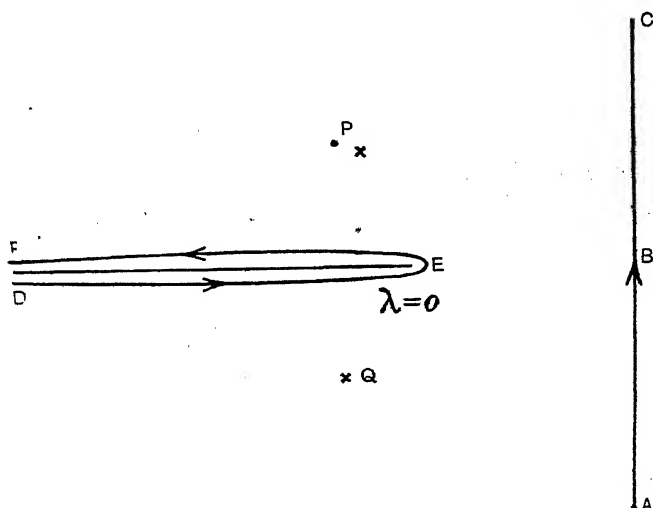
$$1 - \sqrt{\left(\frac{\tau}{\pi t}\right)} \left\{ 1 - \frac{t}{2\tau} + \frac{1 \cdot 3}{2 \cdot 2} \left(\frac{t}{\tau}\right)^2 - \frac{1 \cdot 3 \cdot 5}{2 \cdot 2 \cdot 2} \left(\frac{t}{\tau}\right)^3 + \dots \right\}$$

from which numerical results are easily found when  $t/\tau \geq 10$ .

From the point of view of the complex integral, the first step (expanding in descending powers of  $\lambda\tau$ ) requires that  $\lambda\tau$  shall be greater than 1 (in absolute value): this is satisfied by placing the original path  $ABC$  sufficiently far to the right (by taking in fact  $c\tau > 1$ ). The values of the integrals are found from results originally given by Cauchy: but undoubtedly the most rapid method of reproducing their values is to use Heaviside's formulae\*

$$p^{\frac{1}{2}} = \frac{1}{\sqrt{(\pi t)}}$$

and to operate on this by integration or differentiation.



On the other hand, to obtain the asymptotic series, the path of integration is first bent round from  $ABC$  to  $DEF$  in the diagram; then we can write  $\lambda\tau = -\mu^2$ ,  $\sqrt{(\lambda\tau)} = +i\mu$  on the upper path  $EF$ ,  $\sqrt{(\lambda\tau)} = -i\mu$  on the lower path  $DE$ , and the complex integral becomes

$$1 - \frac{2}{\pi} \int_0^\infty \frac{d\mu}{1 + \mu^2} e^{-\mu^2 t/\tau},$$

where the 1 arises from the integral round  $\lambda = 0$ .

\* An investigation of this formula from the point of view of complex integrals is carried out in § 4 of the second paper quoted. I think there can be no doubt that Heaviside himself regarded this result as the key to his subsequent developments: from his letters, it would seem that the investigation given in *Electromagnetic Theory*, 2, 287-8, is substantially his original method. It will be noted that the integrals used there are the same as those obtained at once from the complex integrals.

Then, if we are content with, say, three terms of the asymptotic series, we may write

$$1 + \mu^2 = 1 - \mu^2 + \mu^4 \quad \frac{\mu^6}{1 + \mu^2}$$

so that the error introduced by using only three terms in the series\* is

$$\frac{2}{\pi} \int_0^\infty \frac{\mu^6 d\mu}{1 + \mu^2} e^{-\mu^2 t/\tau} < \frac{2}{\pi} \int_0^\infty \mu^6 d\mu e^{-\mu^2 t/\tau}$$

which is now seen to be the fourth term of the asymptotic series itself.

At first sight it may seem strange that in this method of calculation no trace is left of the terms in Heaviside's series which contain integral powers of  $p$  (that is,  $\tau p$ ,  $(\tau p)^2$ , etc.): the explanation is that these terms contribute equal amounts to the integrals along  $DE$ ,  $EF$ , and these terms accordingly cancel out in pairs. It is in this sense that we must interpret the formulae

$$p \cdot 1 = 0, \quad p^2 \cdot 1 = 0, \quad p^3 \cdot 1 = 0, \text{ etc.}$$

which usually occur only in asymptotic series.

Let us consider next another example, in which more care is needed.

*Ex. 2. (Electromagnetic Theory, 2, § 244.)*  $f(p) = 1/\{1 + (\tau p)^{\frac{2}{3}}\}$ .

The series in ascending powers of  $t/\tau$ , is derived from

$$\frac{1}{(\tau p)^{\frac{2}{3}}} - \frac{1}{(\tau p)^{\frac{8}{3}}} + \frac{1}{(\tau p)^{\frac{14}{3}}} - \frac{1}{(\tau p)^{\frac{20}{3}}} + \dots$$

and is

$$\frac{4\pi}{3} \left(\frac{t}{\pi\tau}\right)^{\frac{3}{2}} \left\{ 1 + \frac{2 \cdot 2 \cdot 2}{5 \cdot 7 \cdot 9} \left(\frac{t}{\tau}\right)^3 + \frac{2 \cdot 2 \cdot 2 \cdot 2 \cdot 2 \cdot 2}{5 \cdot 7 \cdot 9 \cdot 11 \cdot 13 \cdot 15} \left(\frac{t}{\tau}\right)^6 - \left\{ \frac{1}{3!} \left(\frac{t}{\tau}\right)^3 + \frac{1}{6!} \left(\frac{t}{\tau}\right)^6 + \frac{1}{9!} \left(\frac{t}{\tau}\right)^9 + \dots \right\} \right\}.$$

Heaviside gives a short table derived from this series from  $t/\tau = \frac{1}{2}$  to  $t/\tau = 6$ .

But if we simply expand  $f(p)$  in the form

$$1 - (\tau p)^{\frac{2}{3}} + (\tau p)^{\frac{8}{3}} - (\tau p)^{\frac{14}{3}} + \dots$$

the derived asymptotic series is not sufficient to express the value of the operator. The result given by Heaviside is

$$1 + \frac{\pi}{2} \left(\frac{\tau}{\pi t}\right)^{\frac{3}{2}} \left\{ 1 - \frac{3 \cdot 5 \cdot 7}{2 \cdot 2 \cdot 2} \left(\frac{\tau}{t}\right)^3 + \frac{3 \cdot 5 \cdot 7 \cdot 9 \cdot 11 \cdot 13}{2 \cdot 2 \cdot 2 \cdot 2 \cdot 2 \cdot 2} \left(\frac{\tau}{t}\right)^6 - \dots \right\} - \frac{1}{3} e^{-t/2\tau} \cos(t\sqrt{3/2}\tau)$$

where the presence of the last term could not be naturally foretold without further investigation†.

The explanation of the extra term, from the point of view of the complex integral, arises from the fact that the denominator  $1 + (\lambda\tau)^{\frac{2}{3}}$  vanishes at two points

\* Starting from the known formula

$$\frac{2}{\pi} \int_0^\infty d\mu e^{-\mu^2 t/\tau} = \frac{1}{\sqrt{(\pi t/\tau)}}$$

which is equivalent to Heaviside's  $p^{\frac{1}{2}} = 1/\sqrt{(\pi t)}$ , the reader may apply the process of differentiation to deduce that the following terms agree with Heaviside's calculations from  $p^{\frac{5}{2}}$ ,  $p^{\frac{7}{2}}$ , etc.

† Heaviside's investigation will be found in the same volume, § 448: his earlier methods are given in *Electrical Papers*, 1, 153-169.

( $P, Q$  in the diagram) corresponding to  $\lambda\tau = e^{2\pi i/3}$  or  $e^{-2\pi i/3}$ : and thus the integral along  $ABC$  is equal to that along  $DEF$ , together with the sum of the residues at  $P, Q$ : and these, when combined into a real form, provide the correction found by Heaviside\*. The actual manipulation of the asymptotic series proceeds on lines similar to those adopted in the former example.

These two examples will probably suffice to show how the complex integral acts as a foundation for the symbolic method: on the other hand, the operational process is the more rapid and compact, serving in fact as a kind of shorthand for these more elaborate calculations. I pass to some other points arising out of Dr Sumpner's paper.

In the solution (§ 7) of the equation

$$\frac{\partial^2 \theta}{\partial x^2} = \frac{c}{h} \frac{\partial \theta}{\partial t} = q^2 \theta, \quad \text{if } q = \sqrt{cp/h},$$

it is necessary to distinguish clearly between the two solutions  $e^{-qx}$  and  $e^{+qx}$ , the former being the correct form if  $x$  can extend to  $+\infty$ . But, from the operational point of view, it seems out of the question to attach any particular sign to the symbol  $q$ ; on the other hand, when  $q$  is regarded as representing a multiple of  $\sqrt{\lambda}$  (in the complex integral), the symbol  $q$  will have the same algebraic character as  $\sqrt{\lambda}$ . Now, in the diagram,  $\sqrt{\lambda}$  will be real and positive at the point  $B$ ; thus  $\sqrt{\lambda}$  will have a positive real part at any point along the path  $ABC$  (for  $\sqrt{\lambda}$  will vary continuously and its real part will vanish only when  $\lambda$  is real and negative). Thus we may treat  $q$  as having a positive real part in the formation of our solutions; this will not prevent us from manipulating the path from  $ABC$  to  $DEF$ , when we require to transform the integrals.

Again, in Heaviside's general cable problem, we are led to the formula for  $q$

$$q^2 v^2 = (p + \rho)^2 - \sigma^2,$$

as in equations (25) of Dr Sumpner's paper; and again the distinction between  $e^{-qx}$  and  $e^{+qx}$  is required. Here, however, the cut required (to give a single value for the square-root) does not extend along the whole negative axis, but simply between the points given by  $\lambda = -(\rho + \sigma)$  to  $\lambda = -(\rho - \sigma)$ . Then the value of the square-root (which is positive at the point  $B$ ) is easily seen to be approximately

$$\lambda + \rho - \sigma^2/2\lambda$$

when  $|\lambda|$  is large. Thus again we arrive at the form  $e^{-qx}$ : and when the corresponding complex integral is examined, the exponential term is approximately

$$\exp \left\{ \lambda \left( t - \frac{x}{v} \right) - \frac{\rho x}{v} - \frac{\sigma^2 x}{2\lambda v} \right\}.$$

It follows that, when  $vt < x$ , the path  $ABC$  can be bent out to the right instead of the left, and then the value of the integral is zero; this simple argument replaces

\* Another illustration is given by Heaviside's generalised cosine series (*Electromagnetic Theory*, 3, 198, 218): further examples are given at the second place, one of which, (35), is not quite correct. This was noted by Heaviside as being then "in an experimental stage." The necessary alteration is easily deduced from the complex integral, but need not be written out here.

that given in Dr Sumpner's § 8. When  $vt > x$ , the path of integration may be bent round to the left, and may conveniently be transformed into an ellipse enclosing the cut. The evaluation of the result in Heaviside's formula containing

$$I_0 \{ \sigma \sqrt{(t^2 - x^2/v^2)} \}$$

is not difficult, but requires some preliminary evaluations of definite integrals which would occupy too much space here\*.

Finally, with reference to Heaviside's impulse function of the time (see § 8 of Dr Sumpner's paper) it may not be out of place to remark that the simplest analytical formula for the function is

$$H(t) = \int_{c-i\infty}^{c+i\infty} \frac{d\lambda}{2\pi i \lambda} e^{\lambda t}, \quad (c > 0)$$

which is unity when  $t$  is positive, and zero when  $t$  is negative†. This formula is, in fact, given by writing  $f(p) = 1$  in our general statements and it may be converted into a form of Fourier's integral‡ (not a series).

AUTHOR'S reply: I am glad that my paper has been the cause of such an interesting and valuable communication from Prof. Bromwich. As regards the footnote on page 405, I quite admit that the Bromwich "interpretation explains the success of Heaviside's work in general" and that it illuminates the whole subject. It seems to me, however, that the steps of Heaviside's method still need more explanation than is to be found either in the papers of Bromwich and Jeffreys, who use complex integrals, or in that of J. R. Carson who uses integral equations and restricts his analysis to the field of real quantity. These papers, in my view, set forth independent methods of establishing results such as those of Heaviside, rather than a detailed justification of the Heaviside method in itself.

\* One method is to show that the result depends only on  $(t^2 - x^2/v^2)$ , by a simple change of variable in the definite integral. The value at  $x=0$  is found most quickly by Heaviside's own analysis to involve  $I_0(\sigma t)$ .

† More details on this point will be found in the tract by Dr H. Jeffreys (*Operational Methods in Mathematical Physics*, Cambridge, 1927): see in particular pp. 21-25.

‡ The result (due to Cauchy) is found by bending the path  $ABC$  to the right ( $t < 0$ ), or left ( $t > 0$ ): in the latter case the residue at  $\lambda=0$  has to be included in the formula.

## A HYGROMETER FOR USE IN TIMBER-SEASONING KILNS

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**ABSTRACT.** The hygrometer is of the wet and dry bulb type using mercury-in-steel thermometers. The bulbs and capillaries are enclosed in a steel tube which can be inserted through a hole 3 in. in diameter and explorations up to 12 ft. can be made with it. One dial serves both thermometers, the two pointers being arranged so that one moves over the top face of the dial and the other is brought round from beneath on to the outside edge. An electrically operated fan draws air past the two bulbs. The moistening of the covering over the wet bulb is effected in two ways: (a) by a reservoir, (b) by connexion to an external water supply.

**I**N many industrial processes it is necessary to vary the humidity of the air in a chamber in accordance with a definite schedule.

For timber-drying kilns the common practice has hitherto been to employ the unventilated type of compound spiral thermograph and to carry out the process according to empirical rules worked out as the result of observations with a particular kiln. For the scientific study of timber drying it is, however, essential to obtain data which can be interpreted in terms of definite physical concepts such as relative humidity, temperature, rate of air circulation, etc.

Bourdon Spirals

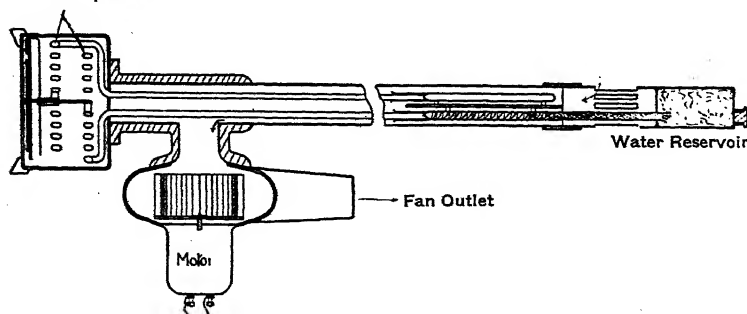
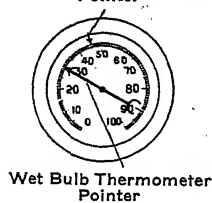


Fig. 1.

Dry Bulb Thermometer Pointer



Wet Bulb Thermometer Pointer

Fig. 2.

The hygrometer shown in Fig. 1 was designed for experimental work in which it was necessary to measure humidities at various distances from the kiln face up to 12 ft. from the walls, which were provided with a series of port-holes. The instru-

ment is of rugged construction, the thermometric elements consisting of two mercury-in-steel thermometers indicating on one dial. The two pointers are arranged as shown in Fig. 2. The steel bulbs and capillary tubes are fixed in a light steel tube 12 ft. in length and perforated at its lower end. Near the point where the tube is attached to the dial an electrically operated fan is fitted on to a branch tube. This fan draws air from the kiln past the thermometer bulbs and capillaries and discharges out to the atmosphere. In the choice of fan consideration must be given to its suitability for this purpose as regards electrical insulation, for moisture is liable to condense in the fan casing and, if it has access to the windings, trouble soon arises.

The wet bulb is sheathed with a layer of muslin which has been treated so as to remove all grease and filling matter. Between the muslin and the bulb a series of fine wires, equally spaced around the bulb, are laid. At the lower end the wires are bunched together and pass into the water reservoir. The function of these wires is to distribute the water supply evenly beneath the covering of the wet bulb. The reservoir was fitted with a prolongation tube leading right up to the bulb; this contained a wick to feed the water along the bundle of wires and the muslin.

The above-described method of keeping the bulb covering wet was found satisfactory for general work. At high temperatures and low humidities it was found advisable to connect the feed pipe to a small-bore tube extending out of the kiln. The tube was connected to a reservoir from which a definite stream of water could be delivered by adjustment of the air pressure until sufficient water had flowed to cause occasional drips to fall from the bulb covering. By the aid of a telescope the condition of the bulb covering could be observed.

The author wishes to thank Mr A. Snow, Observer in the Physics Department, for his assistance.

## REVIEWS OF BOOKS

*Practical Primary Cells*, by A. MORTIMER CODD. Pp. viii + 127, with 53 diagrams. (London: Sir Isaac Pitman and Sons. Ltd.) 5s.

The author, with a wide practical experience of his subject, aims to give within moderate compass working details of the primary cells in most general use in industry and in the laboratory. Chief place is fittingly given to the Leclanché cell, to which over a quarter of the book is devoted. We may read of the Lalande, a cell extensively used in railway work, and of cells less familiar, such as the Bleecke-Love and the Velvo-carbon; and at the end a table of information is supplied in regard to 172 forms of primary cell, with electromotive forces ranging from 0.5 up to 3.14 volts.

In addition to treating the generally recognised characteristics of cells the author directs attention to the practical consequences of the less well known phenomena of endosmosis and the Becquerel effect. The superiority of the single-fluid over the double-fluid cell is emphasised, and preference is expressed for the choice of ferric chloride as a depolariser. We learn with astonishment that primary cells are employed for charging secondary cells!

In respect of the theory of the action of the cell the treatment seems open to criticism. The electro-chemical series is given in the opening chapter, and the impression tends to be conveyed that the electromotive force of a cell is a mere matter of the elements constituting the electrodes. But there remains the important part played by the liquids of the cell; it is possible, for example, to construct a cell in which copper is the negative electrode and zinc the positive, so that copper goes into solution and zinc is deposited as the cell supplies current. Exception must also be taken to the appearance of the obsolete Grotthus hypothesis. In making these remarks, however, it is fair to add that the theory of the voltaic cell presents many difficulties, which hitherto have not been satisfactorily resolved.

D. O.

*Primary Physical Science*, by WILLIAM R. BOWER, B.Sc., A.R.C.S. Pp. 302 with 153 diagrams. (London: Sir Isaac Pitman and Sons, Ltd., 1928.) 5s. net.

Many attempts have been and are being made to write science text-books suitable for the lower forms in secondary schools, for central or modern schools, and for children attending evening classes and technical institutes, but a real success has not yet been achieved. One factor which has determined this lack of success is that writers have offered a form of watered-down secondary school book for children in the other types of school, ignoring the fact that a central or modern school education is not inferior to a secondary school education, but is essentially different from it; the two are not to be measured in the same units.

The book at present under review is well printed on good paper and excellently bound, but the subject-matter and method of treatment belong to the period when science teaching in schools was in its infancy, even though an attempt is made by the author to bring the book up to date by the inclusion of a diagram of the crystal structure of common salt, an account of the internal combustion engine, and some historical notes. Hydrogen is introduced by way of zinc and sulphuric acid, and the properties of gases are printed in heavy type to encourage learning by heart. The introduction to physics is given in a chapter on measurement in which the reader is invited to remember a considerable

number of relations of which "the fluid ounce equals 28.35 cubic centimetres" is typical. In the chapter on heat, temperature is defined in terms of heat in spite of Preston's brilliant treatment in which he shows that temperature, being a percept, is more fundamental than heat, which is a concept.

This is what may be described as a "fact book," and if we judge it by the standards of its type it is good; doubtless it will be successful as a cram book for some elementary examinations, but we feel that even though a child may be filled with scientific facts yet he may still know little or nothing about science. The inclusion of science in the curricula of elementary and central schools cannot be justified if this is science. In the new scheme of education which is developing throughout the country we plead for a true presentation of science with special attention to its relation to the life of the child and of the community; we need first a selection of suitable material and then a presentation suited to the mental development of the child. The consultative committee appointed by the Board of Education, under the chairmanship of Sir W. H. Hadow, has indicated in its recently published report that there is a distinct lack of good first-stage science text-books, but the book under review appears to fall short of the style of text-book which the committee hope will appear, in due course, to fill the gap which they have disclosed.

V. T. S.

*Principles of Radio Communication*, by Prof. JOHN H. MORECROFT, assisted by A. PINTO and Prof. W. A. CURRY. Second edition, thoroughly revised. Pp. xiv + 1001. (New York: John Wiley and Sons, Inc.; London: Chapman and Hall, Ltd., 1927.) 37s. 6d. net.

The science and practice of radio communication have developed so rapidly during the past ten or fifteen years, and now cover such a wide field, that it has become impossible to confine an adequate technical description of the subject within the covers of a single volume. Whatever alteration may take place on the practical engineering side, however, it is unlikely that the fundamental principles of the generation, transmission and reception of electromagnetic waves will be materially changed; and it is with such principles that the somewhat formidable volume compiled by Prof. Morecroft is concerned. It is the second edition of a book with which many radio engineers are already familiar; and although, as mentioned in the preface, two chapters from the first edition have been deleted and a third has been considerably reduced in length, the amount of new material dealt with is such as to bring the present volume up to 1001 pages.

The first chapter of the book describes in a very clear manner the fundamental ideas of the flow of electrons in conductors, the production of electric and magnetic fields and the phenomena associated with the passage of alternating currents in resonant circuits. The electrical properties of a typical radio-frequency circuit, viz. resistance, inductance and capacity, are ably dealt with in the next chapter which concludes with a sound but brief discussion of the problem of screening one circuit from another, for both electric and magnetic fields. Here, as in other portions of the book, there is a very noticeable absence of mention of important British research work, such as that of Butterworth and Howe, on the resistance of coils and the capacity of aërials respectively. Chapter III entitled "Laws of Oscillating Circuits" deals with a branch of the subject which is fundamental to either transmission or reception in radio; but a large portion of the chapter is concerned with damped oscillations, which are rapidly becoming of academic interest only. Further, the fact that Chapter V, entitled "Spark Telegraphy," also deals with an obsolescent portion of the subject suggests that a more drastic curtailment of these chapters might have been carried out. The space so saved might with advantage have been devoted to the intervening fourth chapter which is all too short in its attempt to review the phenomena associated with atmospherics and the propagation of waves over the earth's surface in only forty pages. The sixth chapter is the largest in the book and



may be regarded as a small monograph on the application of thermionics to modern radio communication. In its description of the use of the valve as a rectifier, amplifier and oscillator the chapter is very sound and fairly up-to-date, but it might have been subdivided and re-arranged with some advantage. In this connection it is noticeable that some repetition occurs in the following chapter, which is entitled "Continuous Wave Telegraphy." A good description of the principles of modulating continuous oscillations for use in radio telephony and broadcasting is contained in Chapter VIII. The concluding chapters entitled "Antennae and Radiation" and "Amplifiers" could possibly have been better placed earlier in the book; but otherwise deal usefully with the subjects concerned.

The book is conspicuous throughout for the large amount of experimental data supplied and the reproduction of many excellent oscillograph records illustrating the various phenomena under discussion. These obviously represent the results of the author's own research work, and they form a valuable addition to a text-book which must form a most useful reference volume for every serious technical worker in the field of radio communication. Finally, if the author ever contemplates the somewhat arduous task of compiling a third edition it may be suggested first that a saving of space could be effected by a re-arrangement which avoids certain overlapping between chapters, and also that the value of the book will be increased if more attention is paid to the work carried out in Europe during recent years.

R. L. S. R.

*The National Physical Laboratory: Report for the year 1928.* Pp. vi + 284. (H.M. Stationery Office for the Dept. of Scientific and Industrial Research.) 9s.

This report summarises a year of solid achievement and one in which some important developments have taken place. The first of these concerns the new physics building for which plans were drawn up in 1924 only to be shelved for the time being. We are glad to learn that the contract for the central block of the building has now been placed, and that construction has already begun. This first instalment, when completed, will be occupied by the heat division for which improved conditions are much required. The second is the completion of the high tension building and the erection of the million volt transformers. The report contains a brief description of the building and its plant, and a most striking reproduction of a photograph of the million volt spark. A third is foreshadowed, namely the erection of a compressed air tunnel to meet requirements in aeronautics. This will be begun within the next few months, and its use will enable results obtained from aircraft models to be applied directly to the full-scale machine without the necessity of a scale correction.

In a brief review it would be invidious to single out any one division for special notice. Each year brings its increase in the scope of work upon which the Laboratory is engaged and in the extent to which manufacturers are seeking its assistance. Special reference, however, may be made to the very full programme of work relating to fundamental standards which has been completed and to the increasing volume of experimental work in view under this head. This is work in which the Laboratory has always been a pioneer and which indeed could not be carried out anywhere else in this country.

Lastly, one may hope with the Chairman that a suitable building may soon be available for the sound division, the work of which is susceptible to extraneous disturbances unless specially constructed rooms are available. To those of us who dare not count up the hours we have spent in endeavours to hear lectures and speeches in faulty buildings, the subject of architectural acoustics is one that is very close to our hearts.

# THE PROCEEDINGS OF THE PHYSICAL SOCIETY

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## THE ZEEMAN EFFECT FOR THE ARC SPECTRUM OF GOLD

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**ABSTRACT.** The Zeeman effect for about 50 gold lines has been observed and recorded. The field strength used was about 23,000 gauss. A former assignment of terms to the Au I spectrum by McLennan and McLay has been verified to some extent, but certain modifications have been suggested. Suggestions have also been made as to the identity of a few terms which were not previously identified.

### § 1. INTRODUCTORY

PREVIOUS observations of the Zeeman effect for gold were made by Purvis in 1905\*. He, however, made no measurements of the magnetic resolution of the lines, but merely indicated the type of splitting observed in the magnetic field.

The present work was undertaken after the publication of a paper on the Arc Spectrum of Gold by McLennan and McLay†. They were able to find a number of terms which were predicted by application of the Hund theory to complex spectra. The purpose of this paper is to show the agreements and discrepancies which have been observed between the measured Zeeman effects for the lines, and this former classification. Resolutions of nearly 40 of the stronger lines in the arc spectrum of gold have been observed and measured. Attempts have also been made to obtain patterns for the fainter lines, but the time of exposure necessary in some cases has been prohibitively great.

The estimated intensities of some of the lines, as given in McLennan's paper, were found to be discordant with the intensities as observed on our plates, and in such cases new intensities have been assigned.

\* Purvis, *Proc. Camb. Phil. Soc.* 13, 82 (1905).

† McLennan and McLay, *Proc. Roy. Soc. A.* 112, 95 (1926).

## § 2. OBSERVATIONAL DATA

In the present investigation photographs of the Zeeman effect for lines of Au I ranging from  $\lambda$  2350 to  $\lambda$  6280 have been taken. All the photographs were taken with a 10 ft. concave Rowland grating in an Eagle mounting. The apparatus employed in the production of the magnetic field was an electro-magnet of horse-shoe type, fitted with bored conical poles (semi-angle about  $60^\circ$ ). Only small currents could be passed through the coils of the magnet, as it was not water cooled. For exposures of longer duration than about 30 minutes, a current of not more than 6 amp. was allowable, but for shorter periods currents up to 10 amp. were employed. The current through the magnetising coils was kept constant during an exposure by means of a carbon rheostat.

With the poles very close together (about 1 mm.), a maximum field strength of about 27,000 gauss was obtainable. Under these conditions, however, difficulty arose on account of arcing between the poles themselves. Field strengths of from 22,000–25,000 gauss (with poles 2–3 mm. apart), were much more satisfactorily attained and were generally used in the exposures.

Only an arc in air has been used as a source of light. Some plates were taken with an arc *in vacuo*, produced by the use of a vacuum chamber fitting around the poles, as described by Beals\* in a paper on palladium, but no additional Zeeman components appeared, neither were the patterns more easily measured. Also, by the use of a vacuum arc, the necessary time of exposure was much increased, and in addition trouble was occasioned, since the gold electrodes had to be removed from time to time to be scraped and the vacuum chamber made this removal difficult. It was found that a periodic scraping of the electrodes assisted the arc to burn steadily.

The two arms of the magnet were insulated from one another and were made the positive and negative poles of the arc. In the earlier experiments one pole only was drilled along its axis. Through a brass collar fitted into this hole was threaded an iron rod, into the tip of which a small piece of gold was riveted. Another small piece of gold was fixed upon the solid pole piece of the undrilled arm. The arc was established between the gold pieces. In later experiments, however, both arms were drilled, and through a brass collar fitted into each arm passed an iron rod, with gold tip, as described above. This gave the advantage of the easy removal of both electrodes for scraping purposes, without disturbance of the inter-pole distance. The arc was run on 220 volts.

Difficulty was experienced in maintaining a steady arc between two gold electrodes. A small current had to be used, as otherwise the heat of the arc melted the gold. Two methods were adopted with a measure of success to render the arc steadier. In the first case, it was found that if small quantities of certain salts were fed into the arc at intervals it would burn without attention for a considerable period. The salts actually used were the chlorides of cadmium and calcium. In the second method, one gold and one silver electrode were used. Either of these methods served a double purpose, for, in addition to giving a more stable arc, they also gave

\* Beals, *Proc. Roy. Soc. A.* 109, 369 (1925).

lines on the plates exhibiting Zeeman resolutions suitable for use in calculating the field strength.

All lines except those of wave-length greater than  $\lambda 5100$  were obtained in the third and higher orders. The time of exposure varied from 5 min., in the case of the very strong lines, to  $2\frac{1}{2}$  hours for the weak lines. With these long exposures it was found that nitrogen bands frequently appeared strongly on the plates, and masked the Zeeman effects of the fainter gold lines present in the band. In an attempt to overcome this difficulty the arc was run in an atmosphere of oxygen, but even after repeated attempts with long exposures some of the faint lines have never appeared on the plates. The time during which the current could pass through the magnetising coils was limited by the excessive heating of the coils and iron, with a consequent variation in field strength which blurred the Zeeman patterns.

All photographs were taken at right angles to the direction of the magnetic field. A quartz double-image prism was used to separate the oppositely polarised components of the patterns. The time of exposure when the quartz prism was used was greatly increased, and accordingly it was impossible to obtain the separated *p* and *s* components of some of the weak lines. In some instances a greater number of components was disclosed by its use. For example, the pattern for the line  $\lambda 5064.6$  appeared as a very diffuse doublet without the prism, but with its use the pattern was observed to consist of eight components of type (0.79), 0.57, 1.14, 1.68.

Purvis used a gold spark as a source of illumination, and estimated the strength of field employed at 40,000 gauss. This is undoubtedly an over-estimate, for in certain cases he observed lines as merely broadened, whereas in the present investigation these same lines have been at least partially resolved. It is accordingly concluded that the field strength in this work is greater than that obtained by Purvis. It may also be noted here that whereas he gave the line  $\lambda 3586.70$  as a doublet, or reversal, the present results have shown it to be a triplet of type (0), 1.08. This pattern is shown in the plate.

In most cases complete resolution of the lines into their Zeeman components has not been attained, but the measurements of the unresolved patterns have been helpful in deciding to what degree the classification of terms by McLennan and McLay has been verified. In a number of instances the effects have appeared as pseudo-triplets, or pseudo-quartets. By investigation of the type to which the pattern conforms, the *g*-values of some of the terms have been calculated. From these calculated values it has been possible, in some cases, to suggest modifications in the previous assignment of terms.

### § 3. THE FIELD STRENGTH

In order to calculate the field strength, measurements of Zeeman resolutions of the following lines have been used: the *H* and *K* lines of calcium,  $\lambda 3933.66$  and  $\lambda 3968.46$ , giving resolutions (0.33), 1.00, 1.67, and (0.67), 1.33 respectively; the cadmium lines  $\lambda 5086.06$ ,  $\lambda 4800.09$  and  $\lambda 4678.37$ , giving resolutions (0, .5), 1.0,

1.5, 2.0; (0.5), 1.5, 2.0; and (0), 2.0 respectively; and the silver lines  $\lambda$  3280.66 and  $\lambda$  3382.86, with resolutions (0.33), 1.00, 1.67 and (0.67), 1.33 respectively.

The field strength was calculated from the Lorentz formula:

$$H = d\lambda (\text{normal})/\lambda^2 \cdot a,$$

where

$$a = 4.7 \times 10^{-5} \text{ cm.}^{-1} \text{ gauss}^{-1}.$$

#### § 4. NOTE ON NOTATION

Table 1 is a modified form of one given by McLennan and McLay\* in their paper, and shows the most stable energy states of the gold atom which are involved in its emission spectrum. The system of notation is one which has been adopted by Fowler in his recent papers. Two "families" of terms are shown, each being based upon a definite condition of the core. The same prefix is assigned to all terms arising from the same electron configuration, and the orbital designation of the series electron is adopted as this prefix, which is printed in italics. For example,  $6p \ ^2P_1$

Table 1

(a) Au I

K L M N $I_1 \dots 4_1$	O $5_1 \ 5_2 \ 5_3 \dots$	P $6_1 \ 6_2 \ 6_3 \dots$	Q $7_1 \dots$	R $8_1 \dots$	Electrons in un- closed groups	Adopted prefix	Terms	Series limit Au I term
60 60 60 60 60	2 6 10 2 6 10 2 6 10 2 6 10 2 6 10	1 1 1 1 1			<i>s</i> <i>p</i> <i>d</i> <i>s</i> <i>s</i>	6 <i>s</i> 6 <i>p</i> 6 <i>d</i> 7 <i>s</i> 8 <i>s</i>	$^3S$ $^2P$ $^2D$ $^3S$ $^2S$	$^1S$ $^1S$ $^1S$ $^1S$ $^1S$
60 60 60	2 6 9 2 6 9 2 6 9	2 1 1 1 1			$d^9s^2$ $d^9sp$ $d^9sd$	6 <i>s</i> ' 6 <i>p</i> ' 6 <i>d</i> '	$^3D$ { $^4P$ $^4D$ $^4F$ $^2P$ $^2D$ $^2F$ $^2P_1$ $^2D_1$ $^2F_1$ $^4S$ $^4P$ $^4D$ $^4F$ $^4G$ $^2S$ $^2P$ $^2D$ $^2F$ $^2G$ $^2S_1$ $^2P_1$ $^2D_1$ $^2F_1$ $^2G_1$ }	$^3D$ $^3D$ $^1D$ $^3D$ $^1D$

(b) Au II

K L M N $I_1 \dots 4_1$	O $5_1 \ 5_2 \ 5_3 \dots$	P $6_1 \ 6_2 \ 6_3 \dots$	Terms
60 60	2 6 10 2 6 9		$^3D$ $^1S$ $^1D$

indicates the  $^2P_1$  component due to an electron arrangement in which the moving electron occupies a  $6_2$  orbit. By the use of this prefix a term is completely specified, and so the use of the former dashed terms is unnecessary. Combinations between terms involving only a single electron shift are obtained by application of the ordinary selection rule for azimuthal quantum numbers to the series electron. Thus, a  $6s$  term will combine with a  $6p$ , but not with a  $6d$  (subject, of course, to the inner quantum number restrictions).

\* *Loc. cit.*

The combining properties of terms involving a double electron shift are governed by the azimuthal quantum number rule,  $\Delta k = \pm 1$ , for one electron, and  $\Delta k = \pm 2$  or 0 for the other. These possibilities are indicated by dashing the electron symbols corresponding to the definite families, instead of dashing certain of the terms themselves. Intercombinations between the dashed and undashed terms then take place under the normal rules, for example, a  $p$  term may combine with a  $p'$ , but not with a  $p''$  term.

In the case of different sets of terms arising from the same electron arrangement but based upon a different state of the core, a numerical superscript is applied to the term symbol in order to distinguish the particular state of the core to which it is due. As an example, in the second family of terms shown in Table 1 we get two  $^2D$  terms from the  $6p''$  state of the series electron, one based upon the  $^3D$  and the other upon the  $^1D$  term of the Au II spectrum. To distinguish them, the one based upon the  $^3D$  term of Au II is written  $^2D$ , whereas the one derived from the  $^1D$  term is written with a numerical superscript, thus  $^2D^1$ . This superscript in no way affects the combining properties of the terms.

#### § 5. RESULTS

The measured Zeeman effects for the lines which have appeared on the plates are collected in Table 2. The wave-lengths are as given by McLennan and McLay in their paper on the gold arc spectrum. They are taken mainly from Kayser and Konen's *Handbook*, vol. 7, but a few lines were measured by Bloch, and a few of the very faint lines were measured by McLennan and McLay themselves. In several cases, however, new intensities have been assigned. It was found that the relative intensities of certain groups of lines were not correctly indicated by the assignment of intensities as given by McLennan and McLay in their paper. It should be borne in mind, however, that it is practically impossible to maintain the same scale of intensities throughout when the various members of a multiplet occur in such widely separated regions of the spectrum.

In Table 2 the observed Zeeman effect has been expressed in decimal fractions of the normal separation as shown by lines in a singlet system, and where the pattern exhibited asymmetrical splitting, this has been shown by placing the shorter and longer wave-length components to the left and right respectively of the undisturbed line. Such an asymmetrical pattern is shown in the plate for the line  $\lambda 2352.65$ . The components in parenthesis are those polarised in a direction parallel to the applied field. The strongest component of a pattern is denoted by a black figure. The theoretical Zeeman effects for the lines are also given, these being calculated on the assumption of the combination of terms involved as given in the last column of the table.

#### § 6. DISCUSSION OF RESULTS

In the majority of cases the resolution has not been complete. In spite of this fact, it has been possible to indicate to what degree the former classification may be considered to be satisfactory, and in some instances the incompletely resolved patterns have made it possible to suggest a redistribution of terms.

Table 2

$\lambda$ (Å.U)	Int.	$\nu$ (vac.)	Observed Zeeman effect	Calculated Zeeman effect	Suggested combination
7510.74	5	13310.6			$6p^2P_2-7s^2S_1$
6278.18	5	15923.8	(0), .83	(.07), .73, .87	$6s^2D_3-6p^2P_1$
5956.98	3	16782.4			$6p^2D_3-6d^2D_1$
5862.94	1	17051.6			$6p^2D_3-6d^2D_1$
5837.40	6	17126.5	(.68), 1.31	(.67), 1.33	$6p^2P_1-7s^2S_1$
5721.26	0	17473.8			$6p^2P_2-6d^2D_1$
5655.76	2	17676.2	(0), 1.44	(.03, .09, .14), 1.28, 1.34, 1.40, 1.46, 1.51, 1.57	$6p^2D_3-6d^2D_1$
5261.82	1	18999.6			$6p^2D_3-6d^2D_1$
5147.39	1	19421.9			$6p^2P_2-6d^2D_1$
5064.62	2	19739.4	(.79), .57, 1.14, 1.68	(.27, .80), .53, 1.07, 1.60	$6s^2D_3-6p^2P_2$
4811.61	3	20777.3	(.72), .48, 1.02, 1.55	(.27, .80), .53, 1.07, 1.60	$6p^2P_2-6d^2D_1$
4792.60	8	20859.7	(0), 1.12	(.07, .20), 1.00, 1.13, 1.27, 1.40	$6p^2P_2-6d^2D_1$
4620.70	0	21635.7			$6p^2F_3-6d^2D_1$
4607.35	2	21698.4	(0), 1.22	(.18, .54), .83, 1.19, 1.55, 1.92	$6p^2P_2-6d^2D_1$
4488.26	4	22274.1	(.50), .99, 1.37, 1.69	(.10, .29, .48, .67), .76, .95, 1.14, 1.33, 1.52, 1.72, 1.90	$6p^2P_2-6d^2D_1$
4437.28	1	22530.0	(.58), .84, 1.34	(.17, .51, .86), .51, .86, 1.20, 1.54, 1.89	$6p^2F_3-6d^2D_1$
4315.11	4	23167.9	(0), 1.25	(.07, .20, .33), .91, 1.04, 1.17, 1.30, 1.43, 1.57	$6p^2F_4-6d^2D_1$
4241.84	2	23568.2	Six components equally spaced	(33), 1.00, 1.67	$6p^2P_2-8s^2S_1$
4084.14	2	24478.1	(0), 1.07	(.09, .26), .77, .94, 1.12, 1.29	$6p^2F_3-6d^2D_1$
4065.08	8	24592.8	(0), .87	(.07), .73, .87	$6p^2P_1-6d^2D_1$
4040.95	4	24739.7	(0), 1.19	(.11, .34), .69, .91, 1.14, 1.37	$6s^2D_3-6p^2P_2$
3909.39	2	25572.2	(.90), 1.52	(.47, 1.40), .33, 1.27, 2.20	$6s^2D_2-6p^2P_2$
3897.88	7	25647.7	(0), 1.26		$a-6d^2D_1$
3889.45	1	25703.3			$6p^2D_3-6d^2D_1$
3875.08	1	25800.8			$6p^2D_3-6d^2D_1$
3801.97	1	26294.7			$6p^2P_2-7d^2D_3$
3795.90	4	26336.7	Broadened, with central component	(.07, .20), 1.00, 1.13, 1.27, 1.40	$6p^2P_2-7d^2D_3$
3650.74	3	27383.8	(.68), 1.33	(.67), 1.33	$6p^2P_1-8s^2S_1$
3355.18	2	29796.1	.46	(.27, .80), .53, 1.07, 1.60	$6s^2D_3-6p^2P_2$
3320.14	4	30110.6			$6p^2P_1-7d^2D_3$
3308.31	4	30218.3	(.24, .64), 1.46, 1.85	(.20, .60), .60, 1.00, 1.40, 1.80	$6s^2D_2-6p^2P_2$
3204.74	3	31194.7	(0), 1.28	(.05, .14, .24, .33), 1.00, 1.09, 1.19, 1.28, 1.38, 1.48, 1.57, 1.67	$6p^2F_4-6d^2D_1$
3194.73	2	31292.5			$6p^2F_4-c$
3146.37	1	31773.5			$6s^2D_3-6p^2P_2$
3122.78	9	32013.5	(0), 1.11	(.07, .20), 1.00, 1.13, 1.27, 1.40	$6s^2D_3-a$
3020.22	8	33002.2	(.83), 1.64		$a-6d^2D_1$
2891.96	1	34568.5			$6s^2D_3-6p^2P_2$
2883.46	4	34670.4	(.51), —	(.20, .60), .60, 1.00, 1.40	$6s^2D_3-6p^2P_2$
2748.26	8	36375.9	(0), 1.33	(.02, .06, .10), 1.14, 1.18, 1.22, 1.26, 1.29	$6s^2D_3-6p^2P_2$
2700.90	5	37013.7	(.44), 1.08	(.09, .26, .43), .77, .94, 1.11, 1.28, 1.44	$6s^2D_3-6p^2P_2$
2688.72	5	37181.4	1.27, (0), 1.17	(.03, .09), .77, .83, .89, .94	$6s^2D_3-6p^2P_2$
2675.95	10R	37358.8	(.67), 1.33	(.67), 1.33	$6s^2S_1-6p^2P_1$
2641.49	6	37846.1	1.17, (0), 1.01	(.27, .80), .40, .93, 1.47, 2.00	$6s^2D_3-6p^2P_2$
2590.05	4	38597.7			$6s^2D_3-7p^2P_1$
2544.20	3	39293.4	.80	(.27, .80), .53, 1.07, 1.60	$6s^2D_3-7p^2P_2$
2510.50	3	39820.6	1.74, 0, 1.62	(.29, .86), .51, 1.08, 1.66, 2.23	$6s^2D_3-6p^2P_2$
2427.98	10R	41174.0	Reversed. Six components equally spaced	(.33), 1.00, 1.67	$6s^2S_1-6p^2P_2$
2387.75	4	41867.6	1.77, (0), 1.47	(.11, .34, .57), .86, 1.09, 1.31, 1.54, 1.77, 2.00	$6s^2D_3-6p^2P_2$
2376.25	3	42070.3	1.26, 0, 1.45	(.07, .20), 1.00, 1.13, 1.27, 1.40	$6s^2D_3-6p^2P_2$
2364.57	3	42278.1	Broadened		$6s^2D_3-b$
2352.65	4	42492.2	1.34, 0, 1.03	(0), 1.20	$6s^2D_3-6p^2P_2$
2129.46	2	46945.4	Broadened	(0), 1.20	$6s^2D_3-6p^2P_2$
2126.62	2	47008.2			$6s^2S_1-6p^2P_2$
2021.40	3 +	49454.6			$6s^2D_3-6p^2P_2$
* $\lambda$ vac.					
1951.97	3 +	51230.3			$6s^2S_1-6p^2P_2$
1939.24	2	51566.6			$6s^2D_3-7p^2P_2$
1919.63	4	52093.4			$6s^2D_3-6p^2P_2$
1879.87	3	53195.2			$6s^2D_3-6p^2P_2$
1833.14	3	54551.2			$6s^2D_3-b$
1665.73	0	60033.7			$6s^2S_1-7p^2P_1$
1646.66	0	60729.0			$6s^2S_1-7p^2P_2$

Wave-lengths below  $\lambda$  2000 are by E. W. H. Selwyn.

From incompletely resolved patterns, by a study of the intensity distribution among the components, the  $g$ -values of the terms involved have been calculated. It has been found that in most cases the  $g$ -values are abnormal (*i.e.* they do not conform to the Landé values). A similar departure from Landé values has been noted by Shenstone\* in observations of the Zeeman effect for the copper arc. It is apparently due to the fact that the spectrum is partly of the second rank, *i.e.* it is produced by atoms having two electrons neither in  $s$ -orbits nor in closed groups.

In some cases where the patterns are resolved only as triplets, it has been instructive to resolve the pattern predicted by the use of Landé's  $g$ -values into a theoretical blend triplet. Since the distribution of intensities in a complicated pattern follows a quadratic formula, it is possible to assume the centre of gravity of the pattern to be approximately one-quarter of the way from the strongest to the weakest component. As an example, in the case of the combination  $^2P_2-^2D_3$ , the theoretical pattern is ( $\cdot 07$ ,  $\cdot 20$ )  $1\cdot 00$ ,  $1\cdot 13$ ,  $1\cdot 27$ ,  $1\cdot 40$ . This reduces to a theoretical blend triplet ( $0$ ),  $1\cdot 10$  (approx.). The line  $\lambda\ 3122\cdot 78$ , in which these terms are involved, exhibits a pattern ( $0$ ),  $1\cdot 11$ .

For the sake of clearness, the combinations between the terms have been drawn up in the form of tables. The magnitudes of the terms are those given by McLennan and McLay, with the difference that here the deepest term,  $6s\ ^2S_1$ , has been given its absolute value,  $74461\cdot 0\text{ cm.}^{-1}$ . This term was calculated by McLennan and McLay as the limit of the  $^2P$  series, of which  $6p\ ^2P$  and  $7p\ ^2P$  are two consecutive members in Rydberg sequence.

Table 3 contains combinations between terms based upon a  $d^{10}$  state of the core (Table 1). In the same table are also shown the combinations between the terms  $6p$ ,  $7p\ ^2P$  with  $6s''\ ^2D$ .

Table 3

Term	Term value	$6p\ ^2P_1$ 37102·2	$6p\ ^2P_2$ 33286·8	$7p\ ^2P_1$ 14428·5	$7p\ ^2P_2$ 13732·8
$6s\ ^2S_1$	74461·0	37358·8 (10R)	41174·0 (10R)	60033·7 (0)	60729·0 (0)
$7s\ ^2S_1$	19976·2	17126·2 (6)	13310·6 (5)		
$8s\ ^2S_1$	9718·6	27383·8 (3)	23568·2 (2)		
$6d\ ^2D_3$	12509·5	24592·8 (8)	20777·3 (3)		
$6d\ ^2D_2$	12427·1		20859·7 (8)		
$7d\ ^2D_3$	6991·9	30110·6 (4)	26294·7 (1)		
$7d\ ^2D_2$	6950·1		26336·7 (4)		
$6s''\ ^2D_3$	53026·2	15923·8 (5)	19739·4 (2)	38597·7 (4)	39293·4 (3)
$6s''\ ^2D_2$	65300·2		32013·5 (9)		51566·6 (2)

In so far as measurements of the Zeeman effect have been made upon the lines in Table 3, the classification (due to McLennan and McLay) has been verified. As will be seen from Table 2, lines involving  $P \rightarrow S$ , and  $P \rightarrow D$  transitions give patterns which conform to the theoretical Zeeman effect. In the case of the lines  $\lambda\ 5064\cdot 62$  ( $6s''\ ^2D_3-6p\ ^2P_2$ ) and  $\lambda\ 4811\cdot 61$  ( $6p\ ^2P_2-6d\ ^2D_2$ ) the resolution has been sufficiently complete to fix the nature of these terms without difficulty. The line

\* Shenstone, *Phys. Rev.* 28 (3), 449 (1926).



$\lambda 2544.20$  ( $6s'' {}^2D_2-7p {}^2P_2$ ) gave a Zeeman effect which appeared as a doublet, 0.80, but this was doubtless due to the fact that it was photographed in the fourth order, and that it is in a region where the sensitivity of the plates is diminishing. Moreover, the lines  $\lambda 5065$  and  $\lambda 4812$ , in each of which the transition  ${}^2P_2-{}^2D_2$  is involved, each gave the Zeeman effect as a doublet, 0.8, when the field was of a smaller intensity and when the polarising prism was not used. The lines  $\lambda 6278$  and  $\lambda 4065$  gave incompletely resolved triplets (o), 0.83 and (o), 0.87 respectively, whereas the theoretical blend triplet for  ${}^2P_1-{}^2D_2$  would be (o), 0.87. The pattern for the lines involving the terms  ${}^2D_3-{}^2P_2$  conform to the theoretical blend triplet (o), 1.10. The identity of the  $6s'' {}^2D$  term has thus been verified. The separation of the components of this term is 12274 wave-numbers, and this separation has recently been compared with the separation of the corresponding term in Cu I and Ag I by McLennan and McLay\* in a paper on Au II. It has been shown that the separations are approximately proportional to the squares of the atomic numbers of the elements concerned.

Assuming the Landé  $g$ -values for the  ${}^2P$  terms, the calculated  $g$ 's of  $6s'' {}^2D_2$  and  $6s'' {}^2D_3$  are 0.79 and 1.24 respectively. The corresponding Landé values are 0.80 and 1.20. Unfortunately, only one combination of the term  $6s'' {}^2D_3$  with the  ${}^2P$  terms has been observed in a magnetic field, and so it has been impossible to check the value 1.24 for  $6s'' {}^2D_3$ . This value has been used to calculate the  $g$ 's of terms in combination with it.

Table 4 contains combination lines between the terms arising from the states of the atom represented by  $5d^9 6s^2$  and  $5d^9 6s 6p$ . It is in this table that a rearrangement of terms has been found necessary, since the observed Zeeman effects are not in agreement with the former classification.

Table 4

$j$ of term	$g$ of term	Term suggested	Term value	$6s'' {}^2D_2$ 53026.2	$6s'' {}^2D_3$ 65300.2	Term suggested by McLennan and McLay
2	1.14	$6p'' {}^2P_2$	23230.1	29796.1 (2)	42070.3 (3)	${}^2P_2$
2	1.36	$6p'' {}^4P_2$	27454.0	25572.2 (2)	37846.2 (6)	${}^2D_2$
3	1.23	$6p'' {}^3D_3$	22807.9	30218.3 (4)	42492.3 (4)	${}^2F_3$
2	1.14	$6p'' {}^4D_2$	18355.8	34670.4 (4)	46945.4 (2)	$a_{23}$
3	1.15	$6p'' {}^4D_3$	13205.6	39820.6 (3)	52093.4 (4)	$c_{23}$
4	1.35	$6p'' {}^4D_4$	23432.6		41867.6 (4)	${}^4D_4$
3	.97	$6p'' {}^3F_3$	15844.8	37181.4 (5)	49454.6 (3 +)	$b_{23}$
3	.96	$6p'' {}^4F_3$	28286.5	24739.7 (4)	37013.7 (5)	${}^3D_3$
4	1.27	$6p'' {}^4F_4$	28924.3		36375.9 (8)	${}^4F_4$
		$a ({}^4P_3^2)$	32298.0		33002.2 (8)	${}^2F_4$
		$b$	10748.4	42278.1 (3)	54551.2 (3)	$d_{23}$

Table 5

Term	Term value	$6p'' {}^2P_2$ 23230.1	$6p'' {}^4P_2$ 27454.0
$6s {}^2S_1$	74461.0	51230.3 (3 +)	47008.2 (2)

\* McLennan and McLay, *Trans. Roy. Soc. Can.* 22, 103 (1928).

Table 5 gives two lines produced by combination of the deepest term of the spectrum,  $6s\ ^2S_1$ , with two of the terms of Table 4. McLennan and McLay gave a third line,  $\lambda\ 1879\cdot13$  ( $\nu = 53198\cdot5$ ), as being a combination between  $6s\ ^2S_1$  and another term of the  $5d^9\ 6s\ 6p$  configuration. The magnitude of this other term was found by assuming  $\lambda\ 3146\cdot37$  ( $\nu = 31773\cdot5$ ) to be produced by its combination with  $6s''\ ^2D_2$ . This gives the magnitude of the term as  $21252\cdot7\text{ cm.}^{-1}$ , which in combination with  $6s\ ^2S_1$  gives  $\nu = 53208\cdot3$ . A new measurement of the former  $\lambda\ 1879\cdot13$  is given by Selwyn as  $\lambda\ 1879\cdot87$  (in *vaxus*), with  $\nu = 53195\cdot2$ . The discrepancy between these observed and calculated wave-numbers is thus 13, which is much too great for  $\lambda\ 1879\cdot87$  to be justly claimed as the combination in question. It has accordingly been omitted. The inclusion of  $\lambda\ 3146\cdot37$  in Table 4 then becomes a speculation, and has also been omitted. The term  $21252\cdot7\text{ cm.}^{-1}$  may have no real significance.

McLennan and McLay suggested that the lines  $\lambda\ 2748\cdot26$  ( $\nu = 36375\cdot9$ ) and  $\lambda\ 2387\cdot75$  ( $\nu = 41867\cdot6$ ) involved the terms  $^4F_4$  and  $^4D_4$  in combination with  $^2D_3$ , but they were uncertain as to which was the deeper term. The present work has shown  $^4F_4$  to be deeper than  $^4D_4$ . From the Zeeman pattern obtained for the line  $\lambda\ 2748$  a  $g$ -value of 1.27 for  $6p''\ ^4F_4$  has been calculated. The Landé  $g$  is 1.24. The calculated  $g$ -value for  $6p''\ ^4D_4$  is 1.35, and the Landé  $g$  is 1.43. It is considered that two other components of the  $6p''\ ^4D$  term are also present in combination with  $6s''\ ^2D$ , these being  $6p''\ ^4D_3$  ( $13205\cdot6\text{ cm.}^{-1}$ ) and  $6p''\ ^4D_2$  ( $18355\cdot8\text{ cm.}^{-1}$ ). Assuming this classification, the  $6p''\ ^4D$  term is seen to be partially inverted. The relative intensities of the lines in question support this classification. The calculated  $g$ -values for  $^4D_3$  and  $^4D_4$  are 1.15 and 1.14 respectively, whereas the Landé values for these terms are 1.37 and 1.20 respectively. There has been no check on this value for  $^4D_3$ , since the magnetic resolution of only  $\lambda\ 2510\cdot50$  ( $\nu = 39820\cdot6$ ), itself a faint and rather nebulous line, was obtainable. The line  $\lambda\ 1919$  is in a region inaccessible to Zeeman measurements.

The term  $28286\cdot5\text{ cm.}^{-1}$  has been designated as  $6p''\ ^4F_3$ , having a  $g$ -value of 0.94 (Landé value, 1.03). The intensities of the lines formed by the combination  $6p''\ ^4F_{3,4}$  with  $6s''\ ^2D$  support this arrangement.

The  $j$  of the term  $23230\cdot1$  must be 2 or 3, since it combines with both  $^2D_2$  and  $^2D_3$ . This present investigation has shown that the Zeeman effect for  $\lambda\ 3355$  ( $\nu = 29796\cdot1$ ) is a faint pseudo-doublet, and  $\lambda\ 2376$  ( $\nu = 42070\cdot3$ ) is a triplet. Hence the  $j$  of the term must be 2. The calculated  $g$  is 1.14, and the term is given as  $6p''\ ^3P_2$ , which is in agreement with the former classification by McLennan and McLay. Similarly, the  $j$  of the term  $27454\cdot0$  must be 2, since  $\lambda\ 3909$  ( $\nu = 25572\cdot2$ ) exhibits a pseudo-quartet (0.90) 1.52 (indicating that the  $j$ 's of the combining terms are equal), and  $\lambda\ 2641$  ( $\nu = 37846\cdot1$ ) exhibits a triplet (0) 1.09 (indicating unequal  $j$ 's). The calculated  $g$  of the term is 1.36. It is suggested that the term involved may be  $6p''\ ^4P_2$ . If this is so, then Table 5 shows two lines produced by combination of  $6p''\ ^3P_2$  and  $6p''\ ^4P_2$  with  $6s\ ^2S_1$ .

In the case of the term  $22807\cdot9$  the magnetic resolution of the lines produced by combination of this term with  $6s''\ ^2D$  has been sufficiently complete to decide its

nature fairly definitely as  $6p'' {}^2D_3$ . The pattern for the line  $\lambda 3308$  ( $6s'' {}^2D_2$ – $6p'' {}^2D_3$ ) is reproduced in Plate 1. The calculated  $g$ -value for the term  $6p'' {}^2D_3$  is 1.23, as compared with the Landé value 1.20. McLennan and McLay formerly classified this term as  ${}^2F_3$ , but the observed Zeeman effects do not conform to this view. A calculated  $g$  of 0.97 for the term 15844.8, which must have a  $j$ -value of 3, from consideration of the type of Zeeman effect, suggests the probability of its being  $6p'' {}^2F_3$ .

Special attention is drawn to the term 32298.0. The line  $\lambda 3029$  ( $\nu = 33002.2$ ) gives a Zeeman effect which has been measured as (0.83), 1.64. The pattern in question is reproduced in Plate 1. It is seen to be quite definitely a pseudo-quartet, from which it appears that the term 32298.0 should have a  $j$  equal to 3, since only combinations between terms of equal  $j$  give pseudo-quartets. Assuming this value of  $j$ , the calculated  $g$  of the term is 1.57, which would indicate  $6p'' {}^4P_3$ . In opposition to this view is the fact that no combination of this term with  $6s'' {}^2D_2$  has been found, whereas if the term is actually  ${}^4P_3$  it should occur quite strongly, and would be in an easily observed region. Further evidence against a  $j$ -value of 4 is obtained by observation of the Zeeman effect for  $\lambda 3898$  ( $\nu = 25647.7$ ), in Table 6, which is produced by combination of this same term with one of value 6650.2. This latter term has been fairly definitely fixed as  $6d'' {}^4D_4$ . Hence if the  $j$  of the term 32298.0 were 4, the Zeeman effect should be a pseudo-quartet, whereas it was observed as a triplet (0), 1.26, which points to the inequality of the  $j$ 's of the combining terms. The observed triplet is in agreement with the assumption of the transition  $6p'' {}^4P_3$ – $6d'' {}^4D_4$ . McLennan and McLay gave the term as being  ${}^2F_4$ , but this does not agree with the observed Zeeman patterns. The combination  ${}^2D_3$ – ${}^2F_4$  should give a blend triplet (0), 1.07 (approx.), whereas the observed pattern was (0.83), 1.64, as previously stated.

No observations of the Zeeman effect for the lines  $\nu = 42278.1$  and  $\nu = 54551.2$  have been possible, and so it is impossible to suggest the identity of the term 10748.4.

Table 6 shows combinations between  $6p''$  terms and  $6d''$  terms. McLennan and McLay did not suggest the identity of these  $6d''$  terms. From a consideration of the magnetic resolutions exhibited by lines in this table, the suggestions are

Table 6

Term	Term value	$6d'' {}^4D_4$ 6650.2	$6d'' {}^4D_3$ 5756.4	$6d'' {}^4D_2$ 3808.3	$6d'' {}^4F_5$ – 2270.5	$c$ – 2368.2
$6p'' {}^2P_2$	23230.1		17473.8 (0)	19421.9 (1)		
$6p'' {}^4P_3$	27454.0		21698.4 (2)			
$6p'' {}^2D_3$	22807.9		17051.6 (1)	18999.6 (1)		
$6p'' {}^4D_4$	23432.6	16782.4 (3)	17676.2 (2)		25703.1 (1)	25800.8 (1)
$6p'' {}^4F_5$	28286.5	21635.7 (0)	22530.0 (1)	24478.1 (2)		
$6p'' {}^4F_4$	28924.3	22274.1 (4)	23167.9 (4)		31194.7 (3)	31292.5 (2)
$a$	32298.0	25647.7 (7)			34568.5 (1)	

made that the term 6650.2 is represented by  $6d'' {}^4D_4$  ( $g$ -value = 1.41, Landé  $g = 1.43$ ), and 5756.4 by  $6d'' {}^4D_3$  ( $g$ -value = 1.25, Landé  $g = 1.37$ ). By observation

(a)



Au  $\lambda$  2352.65  
1.34, 0, 1.03

(b)



Au  $\lambda$  2748.26  
(0), 1.33

(c)



Au  $\lambda$  3029.22  
(.83), 1.64

(d)



Au  $\lambda$  3308.31  
(.24, .64), 1.46, 1.85

(e)



Au  $\lambda$  3586.70  
(0), 1.08

(f)



Au  $\lambda$  4315.11  
(0), 1.25

(g)



Au  $\lambda$  4437.28  
(.58), .84, 1.34

(h)



Au  $\lambda$  4488.26  
(.50), .99, 1.37, 1.69

(k)



Au  $\lambda$  4607.35  
(0), 1.22

(l)



Au  $\lambda$  5837.40  
(.68), 1.31

(m)



Au  $\lambda$  6278.18  
(0), .83

(n)



Ca  $\lambda$  3933.66  
(.33), 1.00, 1.66

(o)



Ag  $\lambda$  3382.86  
(.66), 1.33

(p)



Cd  $\lambda$  4678.37  
(0), 2.00

(q)



Cd  $\lambda$  4800.09  
(.50), 1.50, 2.00

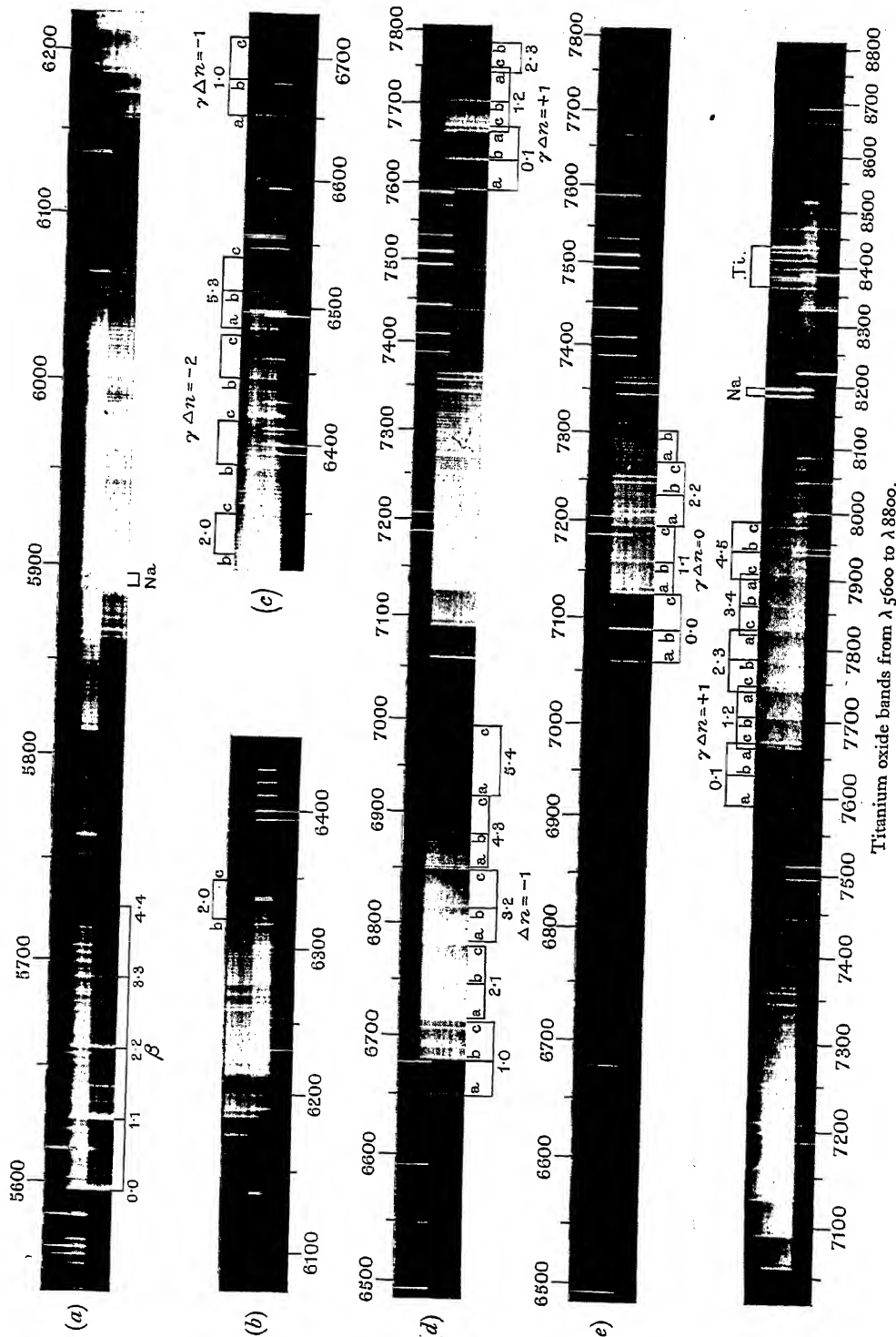
(r)



Cd  $\lambda$  5086.06  
(0, .50), 1.00, 1.50, 2.00

Some typical Zeeman patterns.







of the Zeeman effect for  $\lambda 4084$  ( $\nu = 24478.1$ ) it is suggested that the term  $3808.3$  is probably  $6d''^4D_2$ . The term  $-2270.5$  appears to have a  $j$ -value of 5, and the assignment of  $6d''^4F_5$  to this term is in reasonably good agreement with the observed effect for  $\lambda 3205$  ( $\nu = 31194.7$ ), which is (0), 1.28, whereas the theoretical blend triplet would be (0), 1.48. Owing to the faintness of the other lines involving the term  $-2270.5$ , their magnetic resolutions have not been observable, and so the identity as  $6d''^4F_5$  is in some doubt. No line involving the term designated  $c$  has appeared on the Zeeman effect plates, and so no suggestion is offered for it.

### § 7. SOME GOLD SPARK LINES

In Table 7 are collected a number of lines which have appeared on the Zeeman effect plates of the gold arc but are not directly attributable to Au I. They are apparently spark lines, and probably arose from the regions near the poles of the

Table 7

$\lambda$ (I.A.U.)	$\nu$ (vac.)	Observed Zeeman effect
5230.31 (1n)	19114.0	(0) 1.17
4902.27 (1)	20393.0	(0) .86
*4052.80 (6)	24667.4	(0) 1.05
*4016.07 (5)	24892.9	(0) 1.04
3915.86 (1)	25530.0	1.08
3874.68 (3)	25801.3	(0) 1.09
*3803.99 (6)	26280.8	(0) 1.33
*3633.25 (4)	27515.2	(0) 1.19
3607.50 (1n)	27712.2	(0) 1.34
3553.56 (3)	28132.8	1.41 (0) 1.28
3586.70 (5)	27872.9	(0) 1.08
*3122.50 (5)	32016.4	(0) 1.19
3034.13 (1)	32948.8	(0) 1.22
*2990.26 (5)	33432.2	.86
*2913.51 (10)	34312.8	(0) 1.19

\* Classified as Au II lines by McLennan and McLay.

arc, which were necessarily very close together. Some of these lines, namely those marked with an asterisk, have been assigned to the Au II spectrum by McLennan and McLay†. The wave-lengths and estimated intensities are from Kayser and Konen. The Zeeman effect is expressed in the usual manner.

### § 8. ACKNOWLEDGMENT

In conclusion the authors wish to express their indebtedness and sincere thanks to Prof. A. Fowler, F.R.S., who suggested the investigation, and who has taken an unfailing interest during its progress.

† McLennan and McLay, *Trans. Roy. Soc. Can.* 22, 103 (1928).



# PRESSURE SHIFTS IN THE SPECTRUM OF IONISED NITROGEN

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*Abstract:* The shifting of certain lines in the spectrum N II caused by a change in pressure of the gas in the discharge tube has been investigated. Over 80 lines within the region  $\lambda$  6800– $\lambda$  1850 have been found to shift, and the amount of shift for most of these lines has been determined. The shift is in all cases in the direction of increasing wavelength. The shifts have been discussed in relation to the terms giving rise to the lines concerned and the results have facilitated the identification of three new singlet terms. An enquiry into the nature of the effect leads to the conclusion that it is in the main a Stark effect.

## § 1. INTRODUCTORY

IT has been observed by Fowler\* that certain groups of lines in the spectrum of singly ionised nitrogen, N II, show a broadening and a large shift ( $> 0.5 \text{ \AA.}$ ) towards the red when the spectrum is obtained from a vacuum discharge through a capillary tube, the gas being at a pressure of a few cm. of mercury. The wavelengths from which the shifts were reckoned were those obtained when the pressure of the gas was very low. The effect seemed to call for further investigation, inasmuch as it appeared to be confined to but a small fraction of the spectrum and was remarkable also for the magnitudes of the shifts compared with those usually associated with the "pressure effect." A similar instability in certain groups in the spectra of O II† and O III‡ has also been observed by Fowler.

A more extensive examination of the spectrum of N II has revealed many more lines subject to shift at higher pressures, and the results raise some points of interest. A preliminary investigation into the nature and cause of the effect has also been made.

## § 2. EXPERIMENTAL

The spectrum was obtained from an electric discharge through nitrogen in an ordinary H-type tube having a capillary about 8 cm. long and 1 mm. bore. The tube was excited by a 12 in. induction coil with mercury interrupter. In series with the discharge tube was connected a spark gap the electrodes of which were two brass spheres about 1 cm. in diameter. The distance between the spheres could be varied by a screw adjustment: for most of the photographs this distance was kept at

\* *Proc. Roy. Soc. A.* 107, 37 (1925).

† *Proc. Roy. Soc. A.* 110, 478 (1926).

‡ *Proc. Roy. Soc. A.* 117, 325 (1928).

3.0 mm. A condenser, the capacity of which could be varied but was kept constant for a particular series of photographs, was in parallel with the secondary terminals of the coil.

The method adopted for detecting the shifts was to take two photographs, one at a fairly high pressure (about 5 cm.) and the other at low pressure ( $< 0.1$  cm.), in juxtaposition on the same plate. In this way the shifted lines could be readily picked out. For determining the magnitudes of the shifts, the high pressure was finally chosen to be about 1 cm. This was necessary in order that measurements might be made on close groups, the members of which at higher pressures fused into one another. Although the adoption of this comparatively low pressure made the quantity to be measured smaller, the loss was to a considerable extent compensated for by the increased accuracy in the settings on the lines, due to their comparative sharpness at the lower pressure. In fact it was found that the percentage error involved in measuring the small shifts was of the same order as for the large shifts.

Photographs were taken over the region  $\lambda 6800$ – $\lambda 1850$ , in most cases with adequate dispersion and resolving power. A large dispersion was not always to be desired as the shifted lines became increasingly broad and the error arising from this cause counterbalanced any advantage due to increased dispersion. As it was not possible to photograph the whole of the region  $\lambda 6800$ – $\lambda 1850$  at the same time, it was necessary to ensure that shifts in different regions should be strictly comparable. The range was accordingly divided into the following intervals: (i)  $\lambda 6800$ – $\lambda 3800$ ; (ii)  $\lambda 4000$ – $\lambda 2900$ ; (iii)  $\lambda 3100$ – $\lambda 2400$ ; (iv)  $\lambda 2800$ – $\lambda 2250$ ; (v)  $\lambda 2300$ – $\lambda 1850$ ; so that two overlapping regions had a shifting group common to both. For example, the unstable group common to (i) and (ii) was that at  $\lambda 3800$ ; to (ii) and (iii) the singlet at  $\lambda 3007$ . It was then assumed that if the group at  $\lambda 3800$  showed the same amount of shift on plates (i) and (ii) the conditions under which the spectrum was emitted in each case were the same and all other groups on the two plates could be compared directly with one another.

Region (i) was photographed chiefly on a glass prism instrument having a dispersion of 29 Å./mm. at  $\lambda 6600$  and 5 Å./mm. at  $\lambda 3800$ . (ii), (iii) and (iv) were photographed on a quartz instrument of the Littrow type (Hilger's E. 1) giving a dispersion of 12 Å./mm. at  $\lambda 4000$  and 2 Å./mm. at  $\lambda 2300$ . For (v) a small quartz spectrograph by Bellingham and Stanley, with a mean dispersion of about 7 Å./mm., was used.

All the lines of N II which have been found to shift are given in Table 1 together with the amount of shift. In all cases the shift is to the red.

### § 3. DESCRIPTION OF TABLE I

The wave-lengths and classifications are those published by Fowler and Freeman\*. The notation has been changed to that adopted more recently by Fowler† in his paper on O III. In this notation a term may be generally represented in the form  $nk^rT_j$ , where  $nk$  represents the orbit of the series electron giving

\* *Proc. Roy. Soc. A.* 114, 664 (1927).

† *Proc. Roy. Soc. A.* 117, 317 (1928).

Table 1. Shifts in lines of N II

$\lambda$ (Int.)	Classification	$d\lambda$	$d\nu$	$\lambda$ (Int.)	Classification	$d\lambda$	$d\nu$
6836.2 (1)	$3d^3P_1 - 4p^3S_1$	.87	1.8	2735.0 (1n)	$3p^1S_0 - 5s^1P_1$		
6812.26 (2)	$P_2 - S_1$	.86	1.8	2709.82 (6)			
*6630.5 (2)	$3d^1P_1 - 4p^1S_0$	.43	1.0	2590.91 (4)		.12	1.7
6545.2 (0)	$3d^3D_3 - 4p^3D_2$			2524.55 (1)	$3p^3P_2 - 4d^3D_2$	.13	2.1
6533.0 (1)	$D_2 - D_1$			†2522.51 (1)	$P_1 - D_1$		
6522.3 (0)	$D_2 - D_2$			†2522.27 (4)	$P_2 - D_3$	.17	2.7
6504.9 (2)	$D_3 - D_3$			2520.85 (3)	$P_1 - D_2$	.14	2.2
6492.0 (0)	$D_2 - D_3$	.70	1.6	2520.27 (2)	$P_0 - D_1$	.14	2.2
†6357.0 (3)	$3d^3D_{12} - 4p^3P_{01}$	.54	1.3	2496.88 (4)	$3p^3P_2 - 4d^3P_2$	.15	2.4
†6347.1 (1)	$D_1 - P_1$			2494.02 (1)	$P_2 - P_1$	.15	2.4
†6340.67 (4)	$D_3 - P_2$	.44	1.1	§2493.22 (0)	$P_1 - P_2$	.14	2.3
†6328.6 (1)	$D_2 - P_2$	.45	1.1	2490.37 (2)	$P_1 - P_1$	.13	2.1
				2488.82 (1)	$P_1 - P_0$	.14	2.2
				2488.21 (0)	$P_0 - P_1$		
*6242.52 (5)	$3d^1F_3 - 4p^1D_2$			2461.30 (3)	$3p^1P_1 - 5s^1P_1$	.35	5.8
†6173.40 (3)	$3d^3F_3 - 4p^3D_2$	.50	1.3	2390.90 (2)	$3p^3S_1 - 4d^3P_2$	.18	3.1
†6170.16 (1)	$F_2 - D_1$			2388.24 (1)	$S_1 - P_1$	.18	3.2
†6167.82 (4)	$F_4 - D_3$	.65	1.7	2386.80 (0)	$S_1 - P_0$		
§6150.9 (0)	$F_2 - D_2$	.70	1.8				
§6136.9 (0)	$F_3 - D_3$	.50	1.3	†2321.62 (1)	$3p^3D_3 - 4d^3F_3$	.09	1.7
5104.45 (2)	$3p^1S_0 - 4s^1P_1$	.56	2.2	†2319.90 (1)	$D_2 - F_2$	.09	1.7
4227.83 (3n)	$3p^1P_1 - 4s^1P_1$	.40	2.3	†2317.01 (3)	$D_3 - F_4$	.08	1.5
†3856.07 (3)	$3p^3P_2 - 4s^3P_1$	.37	2.5	†2316.66 (1)	$D_1 - F_2$		
†3855.08 (2)	$P_1 - P_0$	.40	2.7	†2316.46 (2)	$D_2 - F_3$		
3847.38 (3)	$P_1 - P_1$	.33	2.2	2293.40 (2)	$3p^3P_2 - 5s^3P_1$		
3842.20 (3)	$P_0 - P_1$	.34	2.3	2292.72 (1)	$3p^3D_3 - 4d^3D_2$		
3838.39 (5)	$P_2 - P_2$	.33	2.2	2291.67 (2)	$P_1 - P_0$		
3829.80 (3)	$P_1 - P_2$	.32	2.2	2290.31 (1)	$D_3 - D_3$		
					$P_1 - P_1$		
3615.88 (1)	$3p^3S_1 - 4s^3P_0$	.30	2.3	2288.47 (3)	$P_0 - D_2$	.17	3.2
3609.09 (2)	$S_1 - P_1$	.30	2.3		$P_2 - D_2$		
3593.60 (3)	$S_1 - P_2$	.27	2.1	2286.73 (4)	$P_2 - P_2$		
					$D_1 - D_1$	.26	4.9
				2283.70 (2)	$D_2 - D_3$		
3331.32 (3)	$3p^3D_2 - 4s^3P_1$	.23	2.1		$P_1 - P_2$	.27	5.2
3330.30 (2)	$D_1 - P_0$						
3328.79 (4)	$D_3 - P_2$			*2206.10 (3)	$3p^1D_2 - 4d^1D_2$		
3324.58 (2)	$D_1 - P_1$	.22	2.0	2203.72 (1)	$3p^3S_1 - 5s^3P_0$		
3318.14 (2)	$D_2 - P_2$	.28	2.5	2197.58 (2)	$S_1 - P_1$		
					$S_1 - P_2$		
3006.86 (7)	$3p^1D_2 - 4s^1P_1$	.20	2.2	2096.79 (3)	$3p^3D_2 - 5s^3P_1$		
2897.49 (3n)				2096.16 (2)	$D_1 - P_0$		
2892.86 (4n)				2095.47 (6)	$D_3 - P_2$		
2885.25 (6n)				2094.12 (2)	$D_1 - P_1$		
2884.25 (2n)				2091.20 (3)	$D_2 - P_2$		
2879.73 (4n)							
2877.66 (2n)				*1990.99	$3p^1D_2 - 5s^1P_1$		
2823.67 (4)		.06	0.8	*1886.82 (4)	$3s^1P_1 - 4p^1S_0$		
*2799.20 (4)	$3p^1P_1 - 4d^1D_2$	.16	2.1	*1877.97 (2)	$3s^3P_1 - 4p^1S_0$		
				*1868.50 (1)	$3s^1P_1 - 4p^1D_2$		

\* Classified by author. In the case of  $\lambda$  2206 the original classification of Fowler and Freeman,  $3p^3S_1 - 5s^3P_0$  is adopted in part. The additional combination yielding a line in this position explains the anomalous intensities in the triplet.

† Recently classified by L. J. Freeman to whom the author is indebted for the use of unpublished results.

‡ Not very well resolved at high pressure.

|| Confused with band lines.

§ Very faint at high pressure.

A. Unclassified multiplet.

rise to the term (e.g.  $3s$ ,  $3p$ ,  $3d$ ; the letters  $s$ ,  $p$  and  $d$  representing the azimuthal quantum numbers 1, 2 and 3;  $r$  is the multiplicity, T the term type (S, P, D, etc.) and  $j$  the inner quantum number. For instance, a triplet P term arising from a  $3a$  orbit would be represented by  $3p^3P_{012}$ .

The relation of the earlier to the present notation is therefore as follows:

$$\begin{array}{lll}
 1^3P_{012}' = 3s^3P_{012} & 1^3D_{123}' = 3p^3D_{123} & 1^3F_{234}' = 3d^3F_{234} \\
 1^1P_1' = 3s^1P_1 & 2^3P' = 3p^3P & 1^3D' = 3d^3D \\
 1^3P' = 2p^3P & 1^3S_1' = 3p^3S_1 & 1^3P''' = 3d^3P \\
 1^1D_2' = 2p^1D_2 & 2^1D_2' = 3p^1D_2 & 1^1F_3' = 3d^1F_3 \\
 1^1S_0' = 2p^1S_0 & 1^1P_1' = 3p^1P_1 & 1^1D_3' = 3d^1D_2 \\
 & 2^1S_0' = 3p^1S_0 & 1^1P_1''' = 3d^1P_1 \\
 \\ 
 2^3P' = 4s^3P & 2^3D' = 4p^3D & 2^3F' = 4d^3F \\
 2^1P_1' = 4s^1P_1 & 3^3P' = 4p^3P & 2^3D' = 4d^3D \\
 & 2^3S_1' = 4p^3S_1 & 2^3P''' = 4d^3P \\
 3^3P' = 5s^3P & 3^1D_2' = 4p^1D_2 & 2^1F_3' = 4d^1F_3 \\
 3^1P_1' = 5s^1P_1 & 2^1P_1' = 4p^1P_1 & 2^1D_3' = 4d^1D_2 \\
 & 3^1S_0' = 4p^1S_0 & 2^1P_1''' = 4d^1P_1
 \end{array}$$

It will be observed that most of the lines which shift have been classified, the chief exception being the group marked *A*. Unfortunately this group is very diffuse even at low pressures and although a shift could be seen with the unaided eye no measurements have yet been made. The remaining lines are probably singlets: further reference to these will be made later.

In some instances the amount of shift is given for only a few members of a multiplet. This was largely due to the fact that at the high pressure the line spectrum was always accompanied by a faint continuous spectrum and as the shift was accompanied by a broadening of the lines some of the fainter lines became practically undistinguishable against the continuous background and in any case would not allow of measurement. No measurements have yet been made on any of the lines below  $\lambda$  2290. This was due partly to the small separations of the members of the multiplets and partly to the small amount of shift in Å. units.

It will be observed that in cases where the lines of a multiplet are well separated the shifts of the separate lines are equal within the limits of experiment.

#### § 4. THE TERM SHIFT

It has been found that all lines arising from transitions between orbits for which  $n \leq 3$  (i.e. the value of  $n$  in the general term  $nk^rA_j$ ) are steady as far as could be detected by the method employed, while all lines associated with orbits for which  $n > 3$  are unsteady. It seems reasonable on this evidence to assume that orbits for which  $n \leq 3$  are themselves stable (or at most affected to a small and equal extent) and that the orbits for which  $n > 3$  are the ones affected. The only transitions so far observed involving  $n > 3$  are  $n = 5$  to  $n = 3$  and  $n = 4$  to  $n = 3$ , the transition  $n = 5$  to  $n = 4$  being outside the range of wave-lengths here investigated. Assuming the terms having  $n \leq 3$  to be stable, it follows that the shift of any of the lines here considered will represent the amount by which the upper term is affected. This we may conveniently call the "term shift." It is unfortunate that the observable transitions are so limited as the measurement of shifts, in lines arising from orbits for

which  $n = 4, 5, 6$ , etc., combining with others for which  $n > 3$ , would provide a valuable check on the assumption that the shift is a property of the terms and also on the actual values of the term shifts. For instance,  $4p\ ^3S_1-5s\ ^3P_1$  would involve two unsteady terms, the lower of which shows a shift of  $1.8\text{ cm.}^{-1}$  while the upper shows a shift of  $5.2\text{ cm.}^{-1}$ . This line should therefore show a shift of  $5.2\text{ cm.}^{-1} - 1.8\text{ cm.}^{-1} = 3.4\text{ cm.}^{-1}$ .

In the case of a multiplet, the average of the shifts of the separate lines is taken as the term shift, those lines for which measurements are less accurate being omitted in arriving at the average. The fact that no systematic variation of shift in the different members of a multiplet has been detected shows that if there is any variation of term shift with inner quantum number it must be small.

As the shift is to the red in all cases, the change corresponds to an increase in the term value, the deepest term being assumed to have the highest value. That is, it corresponds to a depression of the electron level such as would be caused by a shrinking of the orbit.

Table 2. Term shifts

Term	$\Delta\nu$ (i)*	$\Delta\nu$ (ii)†	Ratio (ii)/(i)
$4s\ ^3P$	2.2	4.6	2.1
$4s\ ^1P$	2.2	4.4	2.0
$4p\ ^3D$	1.6		
$4p\ ^3P$	1.2		
$4p\ ^3S$	1.8		
$4p\ ^1D_2$	2.2		
$4p\ ^1S_0$	1.0		
$4d\ ^3F$	1.6		
$4d\ ^3D$	2.2	4.1	1.9
$4d\ ^3P$	$\begin{cases} 2.3 \\ 3.1 \end{cases}$	$\begin{cases} 4.6 \\ 5.8 \end{cases}$	$\begin{cases} 2.0 \\ 1.9 \end{cases}$
$4d\ ^1D_2$	2.1		
$5s\ ^3P$	5.2		
$5s\ ^1P$	5.8	11.5	2.0

\* Pressure approximately  $0.7\text{ cm.}$

† Pressure approximately  $2.0\text{ cm.}$ , the spark gap being slightly different from (i).

Table 2 gives the shifts corresponding to the different terms. For some of the lines in the spectrum measurements have been made at two different pressures. The corresponding term shifts are included in Table 2, and it will be seen that the ratios of the shifts at the two pressures are practically equal, the shift increasing as the pressure increases.

The terms of N II predicted by the theory of Heisenberg and Hund are shown in Table 3. Transitions giving rise to unsteady lines are shown by means of arrows, broken in order to insert the term shift. For completeness the transitions between terms arising from the  $3_1$  orbit and the  $3_2$  orbit have been included in the scheme, and their stability is indicated by attributing to them zero shift. It is to be borne in mind that these numbers do not represent any absolute property of the terms, but indicate the relative effect on the different terms. For by increasing the pressure

Table 3. Transitions and corresponding shifts

K	L	M	N	O		Triplet Terms	Singlet Terms
1 <sub>1</sub>	2 <sub>1</sub> 2 <sub>2</sub>	3 <sub>1</sub> 3 <sub>2</sub> 3 <sub>3</sub>	4 <sub>1</sub> 4 <sub>2</sub> 4 <sub>3</sub> 4 <sub>4</sub>	5 <sub>1</sub>			
2	2 2				2 <sub>2</sub> 2 <sub>2</sub>	2p	<sup>1</sup> D <sub>2</sub> <sup>1</sup> S <sub>0</sub>
2	2 1	1			2 <sub>2</sub> 3 <sub>1</sub>	3p	<sup>1</sup> P <sub>1</sub>
2	2 1		1		2 <sub>2</sub> 3 <sub>2</sub>	3p	<sup>1</sup> D <sub>2</sub> <sup>1</sup> P <sub>1</sub> <sup>1</sup> S <sub>0</sub>
2	2 1			1	2 <sub>2</sub> 3 <sub>3</sub>	3d	<sup>1</sup> F <sub>3</sub> <sup>1</sup> D <sub>2</sub> <sup>1</sup> P <sub>1</sub>
2	2 1		1		2 <sub>2</sub> 4 <sub>1</sub>	4s	<sup>1</sup> P <sub>1</sub>
2	2 1			1	2 <sub>2</sub> 4 <sub>2</sub>	4p	<sup>1</sup> D <sub>2</sub> <sup>1</sup> P <sub>1</sub> <sup>1</sup> S <sub>0</sub>
2	2 1			1	2 <sub>2</sub> 4 <sub>3</sub>	4d	<sup>1</sup> F <sub>3</sub> <sup>1</sup> D <sub>2</sub> <sup>1</sup> P <sub>1</sub>
2	2 1			1	2 <sub>2</sub> 4 <sub>4</sub>	4f	<sup>1</sup> G <sub>4</sub> <sup>1</sup> F <sub>3</sub> <sup>1</sup> D <sub>2</sub>
2	2 1			1	2 <sub>2</sub> 5 <sub>1</sub>	5s	<sup>1</sup> P <sub>1</sub>

in the discharge tube, leaving the primary electrical conditions unchanged, a particular term shift is altered but, as shown in Table 2, the other terms are likewise affected. The question of the dependence of the shift on the pressure will be considered more fully later.

### § 5. RELATION BETWEEN TERMS AND TERM SHIFTS

A study of the relationships between shifts in various orbits is limited in the case of N II by the fact that no sequence of terms has been found which possesses more than three members. The first member is unaffected by the increase in pressure and therefore only two term shifts have been found for any Rydberg sequence. The results for these, however, do show that the shifts for terms arising from  $n = 5$  are definitely greater than those for which  $n = 4$ , and as those for which  $n = 3$  are zero a progressive increase of shift for increasing values of  $n$  is indicated.

Terms have been found arising from  $n = 4$ ,  $k = 1, 2, 3$ ,  $k$  being the azimuthal quantum number. The shifts corresponding to these terms have been obtained, but their dependence on the value of  $k$  is not evident.  $4s^3P$  combines with  $3p^3D$ ,  $3p^3P$  and  $3p^3S_1$ , and in each case the shift is  $2.2 \text{ cm.}^{-1}$ , see Table 3. This in itself lends support to the assumption that the terms arising from  $n = 3$  are steady or equally affected. The corresponding singlet terms behave in a similar way, the shifts being practically the same as for the triplets. For  $k = 2$  the values of the term shifts are all lower than for  $k = 1$ , with the exception of the singlet term  $4p^1D_2$ .  $4p^3D$  combines with  $3d^3F$  and  $3d^3D$  and in each combination shows the same shift. The

other transitions associated with this orbit show different shifts, those for the triplet terms being greater than that for the singlet. For  $k = 3$  the term shifts are practically equal to those for  $k = 1$ , the exception being  $4d^3F$ . A peculiarity arises in connection with  $4d^3P$ . This term combines with  $3p^3P$  and  $3p^3S_1$ , but the groups of lines resulting from these combinations show different shifts. This would be explained if the deeper terms were unequally affected. But when the deeper terms are in combination with  $3s^3P$  neither shows any shift, and in combination with  $4s^3P$  the shifts are the same. Measurements on these groups showing unequal shifts were rather difficult, but the difference is thought to be real and not due to errors of measurement. At two different pressures, Table 2, the values obtained for the shifts were quite different for each combination.

#### § 6. APPLICATION TO THE IDENTIFICATION OF TERMS

Although no very definite regularities have been found in the term shifts, the following rough generalisations may be made with respect to the triplet terms: (i) groups associated with  $n$  for the upper term  $\leq 3$  are steady; (ii) shift increases as  $n$  increases; (iii) terms arising from  $4_1$  and  $4_3$  orbits show a greater effect than those from  $4_2$  orbits.

These rules can now be applied to the remaining lines which have not as yet been classified, and may indicate the orbits concerned in the production of the lines. For instance, within the range considered, all the multiplets that shift have already been classified with the exception of the multiplet marked *A*. That is to say, if any of the remaining lines form multiplets they are probably associated with orbits for which  $n \leq 3$ . Most of these lines have recently been classified by L. J. Freeman\* and are found to belong to the quintet system. For the terms concerned in their production in no case is  $n$  greater than 3 for a steady group. The quintet system differs from the singlet and triplet systems in that the core has 2 electrons in  $1_1$  orbits, 1 in a  $2_1$  orbit, and 2 in  $2_2$  orbits. The series electron assumes successively the orbits  $2_2$ ,  $3_1$ ,  $3_2$ , etc. It is interesting to note that the change in the state of the core does not affect the stability of the orbits for which  $n \leq 3$ .

As has already been mentioned, there are a few singlets which shift and as yet are unclassified.  $\lambda 6630.5$  ( $\nu 15077.7$ ) from its wave number suggests that it belongs either to a  $3_3 \rightarrow 3_2$  transition or to a  $4_2 \rightarrow 3_3$  transition. As it shifts, the latter alternative is definitely indicated. If we assume that it corresponds to  $3d^1P_1-4p^1S_0$ †, the value for  $4p^1S_0$  is 36676.8.  $4p^1S_0$  should combine with  $3s^1P_1$ , giving a line at  $\nu 52981.1$ , and as there is a line at  $\nu 52981.5$  the assignment is corroborated. This term should also combine with  $3s^3P_1$ , yielding a line at  $\nu 53228.9$ . There is a line at  $\nu 53231.1$ , giving additional confirmation for the value 36676.8. Assuming  $\lambda 6242.5$  ( $\nu 16014.75$ ) to be  $3d^1F_3-4p^1D_2$ , we obtain a value of 36153.27 for  $4p^1D_2$ . This term in combination with  $3s^1P_1$  should give a line at  $\nu 53504.7$  which is probably represented by the line at  $\nu 53500.8$ .

\* The author is indebted to Mr L. J. Freeman for access to results prior to publication.

†  $3d^1P_1 = 51754.5$ . Value taken from paper by Fowler and Freeman, whence

$$4p^1S_0 = 51754.5 - 15077.7 = 36676.8.$$

Another suggested singlet is  $\lambda 2799.20$  ( $\nu 35714.0$ ) as  $3p^1P_1-4d^1D_2$ , giving  $4d^1D_2 = 28919.8$ , which should combine with  $3p^1D_2$ , yielding a line at  $\nu 45315.3$ . Actually there is a fairly strong line at  $\nu 45314.7$ , superposed on  $3p^3S_1-5s^3P_0$ , which suggests that the term has been correctly identified.

A fairly strong line at  $\lambda 1991.0$  ( $\nu 50216$ ) shows a large shift of the same order as the group at  $\lambda 2290$ . It seemed probable therefore that the upper term would arise from an orbit for which  $n \geq 5$ . Trial showed it to be

$$3p^1D_2-5s^1P_1 (74235.1 - 24018.7 = 50216.4).$$

The results obtained are collected in Table 4.

Table 4

	$4p^1D_2^*$ 36153.27
$3s^1P_1 = 89657.96$ $3d^1F_3 = 52168.02$	53500.8 (1) 16014.75 (5)
	$4p^1S_0^*$ 36676.8
$3s^1P_1 = 89657.96$ $3s^3P_1 = 89905.7$ $3d^1P_1 = 51754.5$	52981.5 (4) 53231.1 (2) 15077.7 (2)
	28919.78
$3p^1P_1 = 64633.77$ $3p^1D_2 = 74235.10$	35713.99 (4) 45314.7 (3)

\* Newly identified terms. Other term values are taken from the paper of Fowler and Freeman.

It seems likely therefore that the method might be useful as a supplement to the main methods of spectrum analysis; firstly by indicating which groups belong to the deeper and which to the higher terms, and secondly by assisting particularly in the identification of singlets, which are usually more difficult to classify than multiplets owing to the absence of characteristic wave-number separations.

## § 7. NATURE AND CAUSE OF SHIFT

Shifts in spectral lines as obtained in an ordinary discharge tube can usually be attributed to one or more of the following causes: (i) Doppler effect; (ii) pressure effect; (iii) current density effect; (iv) Stark effect.

In the present case the lines are broadened and displaced towards the red and the intensity distribution in the shifted line, as far as could be ascertained visually, is symmetrical about the middle of the line. There is no broadening in the direction of decreasing wave length. The shift from the undisturbed position is therefore approximately one-half the width of the shifted line. In the Doppler effect the whole spectrum would be affected, the shift being a function of the wave length. With the excitation employed in the present experiments the effect would probably



be to produce an asymmetrical broadening which would be reversed on changing the direction of the discharge. No such effect was observed, and the conclusion is drawn that the shift is not due to the Doppler effect.

A question next arises as to the possibility of the observed shifts being due to a pure pressure effect, analogous to that observed in arc spectra. In order to find out how far pressure was responsible for the effect, the following observations were made:

(i) The primary current through the induction coil, the capacity and the pressure being kept constant, photographs were taken with the series gap at 3 mm., 4 mm. and 5 mm. The shifts increased with the increasing spark gap, as will be seen from Table 5. It will be noticed that the ratios of the shifts for the two different spark gaps are approximately the same for each group. This showed quite definitely that pressure could not be wholly responsible for the shift.

Table 5. Variation of shift with series gap

Pressure 2.5 cm.				Pressure 1.1 cm.			
Group	Gap = 3 mm. Å.U.	Gap = 5 mm. Å.U.	Ratio 5 mm./ 3 mm.	Group	Gap = 4 mm. Å.U.	Gap = 5 mm. Å.U.	Ratio 5 mm./ 4 mm.
$\lambda$ 3600 (triplet)	.40	.76	1.9	$\lambda$ 3600	.29	.44	1.5
$\lambda$ 3007 (singlet)	.30	.67	2.2	$\lambda$ 3007	.18	.29	1.6
				$\lambda$ 3800 (triplet)	.33	.52	1.5

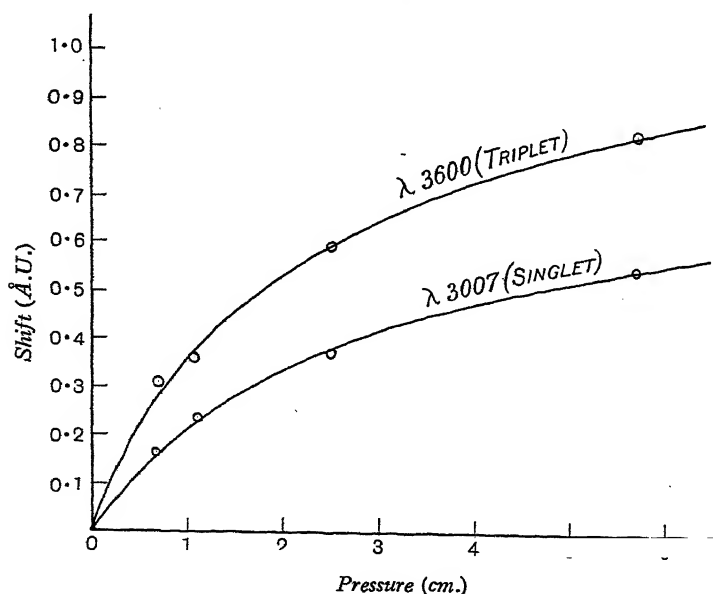


Fig. 1. Relation between shift and pressure (capillary tube).

(ii) The spectrum was obtained from the discharge through nitrogen in a tube of about 4 mm. bore, the electrodes being about 10 cm. apart. For the same pressure the shift under these conditions was much less than in the capillary tube, indicating again that the shift was not entirely due to the pressure.

(iii) With the same tube as in (ii) but with the electrodes only 1 cm. apart a spark was passed in nitrogen at atmospheric pressure, and in this case also the shift was less than in the capillary when the pressure there was 5 cm.

(iv) In the photographs taken with the discharge through a capillary tube it was observed that the lines emitted by the tail-piece of the discharge (*i.e.* the region between the electrode and the entrance to the capillary) showed less shift than those emitted in the capillary. This indicated that in the same tube at the same pressure the shift depended on the region of the discharge in which the line was emitted.

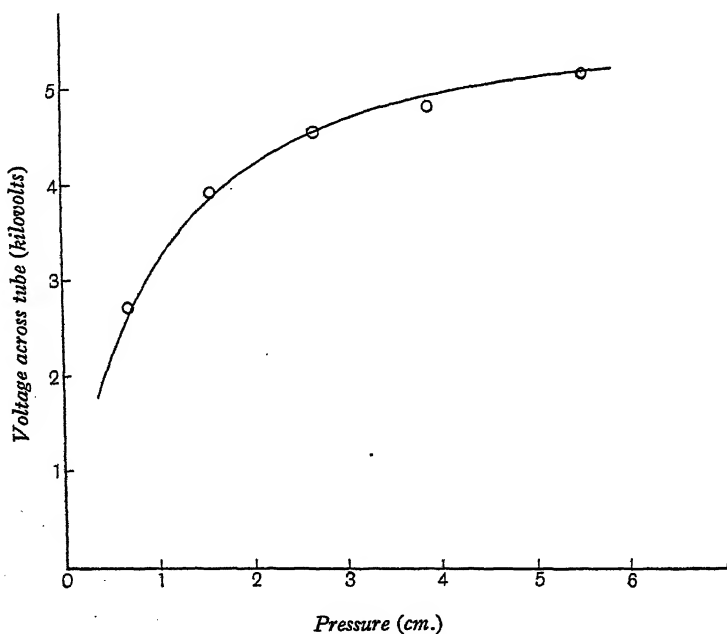


Fig. 2. Relation between voltage across tube and pressure.

(v) The primary current, series gap and capacity being kept constant, photographs were taken at several pressures up to about 5 cm., the discharge tube being of the capillary type. Beyond 5 cm. the lines became too broad and diffuse for measurement. The results are shown graphically in Fig. 1. It is seen that the rate of increase of shift with pressure in the tube is large at first and then gradually diminishes, tending to become quite small and fairly constant.

Experiments were continued with the tube running as in (v), the object being to determine how the electrical conditions varied as the pressure increased. A hot-wire ammeter was included in the secondary circuit but it was found that as measured in this way the current was approximately constant over the range of

pressures employed. This result was due to the integrating effect of the ammeter, which measured only the root-mean-square current; this was approximately constant in virtue of the fact that the primary current was kept constant.

It was decided therefore that the voltage across the discharge tube should be investigated by means of an auxiliary spark-gap. In this way a fairly good value of the peak voltage can be obtained and its variation with the pressure in the tube can be determined quite readily. Fig. 2 shows the graph obtained by plotting voltage against pressure. It bears an obvious resemblance to that in Fig. 1. From these two curves the pressure was eliminated by the derivation of a third curve showing variation of shift with voltage across the tube (Fig. 3).

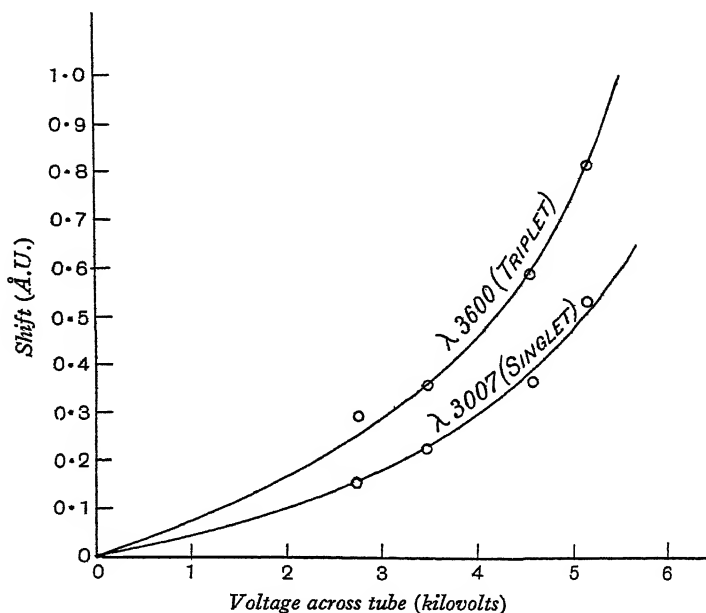


Fig. 3. Showing relation between shift and voltage across tube.

The results of observations made in (i), (ii), (iii) and (iv) showed beyond doubt that the shift was not due merely to an increase in pressure. This conclusion suggested that the change in electrical conditions brought about by a change in pressure was in the main responsible for the effect. The results of observations made in (v) supported this view and in fact seemed to indicate that the shift is in the nature of a Stark effect. In this connection it is interesting to compare the results obtained above with those obtained by Liebert\* on the Stark effect for the principal series of helium (orthohelium). He found that the lines show a displacement to the red and are unresolved, the shift increasing with  $n$  as in the present case. The variation of shift with voltage for helium was as shown in Fig. 4. The similarity between these curves and those for N II (Fig. 3) is most marked, and points once more to the probability that the "pressure effect" in N II is mainly a Stark effect.

\* *Ann. d. Phys.* 56, 593 (1918).

On the assumption that this is the case, it is of interest to note the different conditions under which the two effects are observed. For observations of the Stark effect the gas is usually kept at a very low pressure, and it is in the region near the cathode that the effect manifests itself. In the present case the shift increases with the pressure, and observations are made with the pressure at about 1–5 cm.; further, the shift is observed throughout the capillary. The difference in the conditions is more apparent than real, for in the normal case the discharge is uncondensed, and at very low pressures by far the greater part of the potential drop

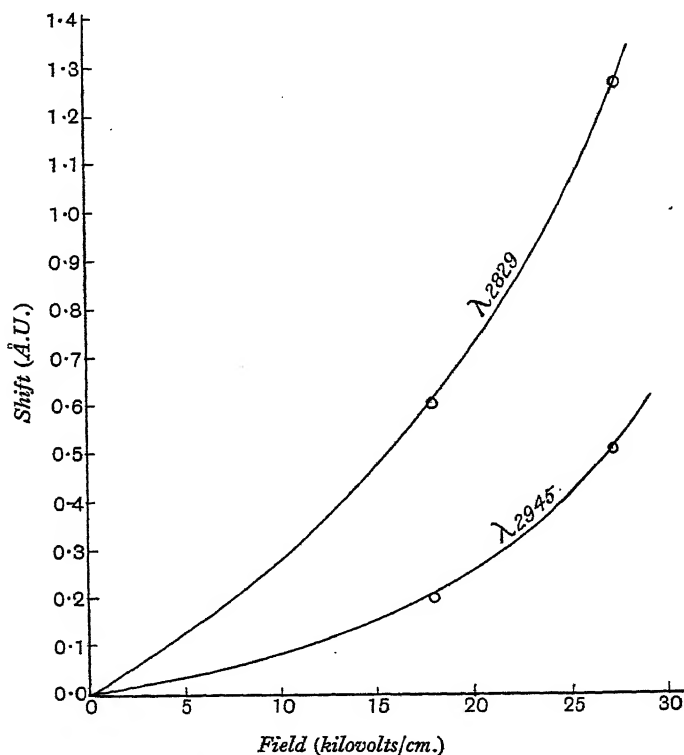


Fig. 4. Liebert's results for helium.

is across the cathode dark space and makes this region particularly suitable for observation of the Stark effect. The spectrum of N II is produced by condensing the discharge and this makes the electric intensity along the tube much more uniform, and in the H-type tube used in the present experiments it is actually greater in the capillary than at the electrodes, as shown by observations on lines emitted by the capillary and tail-piece. So that, although the conditions are different, the determining factor in each case is the electric intensity.

A word of explanation should perhaps be added in regard to the curves. In Figs. 1 and 3 they have been drawn through the origin, although no observations were made at pressures less than 0.7 cm. Fig. 2, showing the relation between voltage and pressure, has not been continued to the origin because at very low

pressures the voltage actually becomes very large owing to the high resistance of the rarefied gas. The passage of curves in Figs. 1 and 2 through the origin must be regarded as an extrapolation of the results at higher pressures and not as showing, necessarily, the true state of affairs in the immediate neighbourhood of the origin.

#### § 8. COMPARISON WITH THE PRESSURE EFFECT IN ARC SPECTRA

Investigations of the pressure effect have been confined chiefly to the examination of arc, spark and furnace spectra at pressures of 1 atmosphere and upwards. Much of the earlier work suffered in definiteness from the inherent difficulty of measuring lines emitted under high pressures. St John and Babcock\* showed that the pole effect may seriously interfere with observations on the pressure effect.

Quite recently the pressure effect for many lines of the Fe arc spectrum has been made the subject of a very careful investigation by Babcock† who took special precautions to eliminate pole effect. The range of pressure was from a vacuum to 1 atmosphere, the errors involved in measuring the shifted lines being thus reduced. The results, in so far as they have a corresponding feature in the present case, may be summarised as follows: (i) Depression of the spectral terms with increase of pressure, the depression being greater for terms of high level than for those of low level and greater for terms of high multiplicity than for those of low multiplicity at the same level; (ii) proportionality between change of pressure and displacement of lines. Babcock also discusses the results of Gale and Adams‡ for titanium and shows that they exhibit the same features.

These results are very similar to those obtained for N II, the chief difference being in the magnitudes of the shifts in the two cases. For whereas in the present case a change in pressure from 0 to 5 cm. produced a shift of the order of 1 wave number, the shift in the Fe lines when the pressure was changed from vacuum to 1 atmosphere was only of the order of  $10^{-2}$  wave number. It has been shown above that the effect in the case of N II is closely allied to a Stark effect and is really not a direct result of pressure. One is naturally led to consider whether this correspondence exists in the case of arc spectra, and, if it does, how much of the pressure effect is due to a Stark effect.

The relation between the pressure effect and the Stark effect is perhaps best considered through the medium of the pole effect. Takaminé§ has shown that there is an exact qualitative agreement between the pole effect and the Stark effect for several lines of the Fe arc spectrum. Quantitatively the agreement is approximately correct. Babcock|| compared his results for the pressure effect with the observed pole effect for many Fe lines. He found that although there is an apparent connection for lines of group d¶ the relation disappears for lines of groups a and b and

\* *Astrophysical Journal*, 42, 1 (1915).

† *Astrophysical Journal*, 67, 240 (1928).

‡ *Astrophysical Journal*, 35, 10 (1912).

§ *Astrophysical Journal*, 50, 23 (1919).

|| *Loc. cit.*

¶ Pressure group classification a, b, c, d of Gale and Adams, *Astrophysical Journal*, 35, 10 (1912).

A further group e has been added by St John and Miss Ware, *Astrophysical Journal*, 38, 209 (1913). Group c has recently been eliminated, *Trans. Int. Astr. Union*, 3, 30 (1929).

in the case of lines of group *e* the shifts are in opposite directions in the two effects. This evidence, Babcock observes, draws a clear distinction between the pole effect and the pressure effect. Assuming then that the pole effect is really a Stark effect, it follows that the pressure effect for the Fe arc spectrum is not a Stark effect. The counterpart in arc spectra to the effect observed in N II appears to be the pole effect rather than the pressure effect.

It has been seen that for N II the shift due to pressure, as such, must be very small compared with the shift due to change in the electrical conditions, but the observations made in the present investigation have not yielded any precise information on this point.

Shifts of lines in the spectra of N III and argon have been found during the present work and these are being investigated together with those in O II and O III.

#### § 9. ACKNOWLEDGMENT

The author wishes to express his thanks to Prof. A. Fowler for suggesting the investigation and for his invaluable advice and criticism during its progress.

## THERMAL DIFFUSION AT LOW TEMPERATURES

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**ABSTRACT.** Measurements of thermal diffusion were made with one side of the apparatus at about  $15^{\circ}$  C. and with the other at temperatures down to about  $-190^{\circ}$  C. For mixtures such as  $\text{H}_2\text{-CO}_2$ ,  $\text{H}_2\text{-N}_2\text{O}$ ,  $\text{H}_2\text{-C}_2\text{H}_4$ , where one constituent easily liquefies, the separation is proportional to  $\log(T_1/T_2)$  throughout the whole range investigated, where  $T_1$  is the absolute temperature of the hot side and  $T_2$  that of the cold side. For mixtures such as  $\text{H}_2\text{-N}_2$ ,  $\text{H}_2\text{-CO}$ ,  $\text{H}_2\text{-A}$ , which can be examined at lower temperatures, the separation is at first proportional to  $\log(T_1/T_2)$ , and then falls below the proportional value. In mixtures of  $\text{N}_2\text{-A}$  this falling off at low temperatures is more pronounced. From these measurements values of  $k_t$ , the ratio of the coefficient of thermal diffusion to the coefficient of ordinary diffusion, can be obtained over a considerable range of temperature. It is suggested that the behaviour at low temperatures may be explained by the fact that real molecules cannot be regarded as point centres of repulsive force only. The general behaviour of a mixture of  $\text{H}_2\text{-O}_2$  is similar to that of  $\text{H}_2\text{-N}_2$  or  $\text{H}_2\text{-A}$ . It is found that thermal diffusion is unaffected by reduction of the pressure to about one-fourth of an atmosphere. This result is in agreement with theoretical prediction.

## § 1. INTRODUCTION

PROF. S. CHAPMAN has shown theoretically how the thermal diffusion\* effect in a mixture of two gases depends upon the temperature gradient applied. If  $\lambda_1$  and  $\lambda_2$  are the proportions by volume of the heavier and lighter gases respectively, so that  $\lambda_1 + \lambda_2 = 1$ , and a temperature gradient is applied in the direction  $x$ , we shall have in the steady state which is reached

$$\frac{d\lambda_1}{dx} = -\frac{d\lambda_2}{dx} = -k_t \cdot \frac{d(\log T)}{dx},$$

where  $T$  is the absolute temperature.  $k_t$ , as defined in the theory, is the ratio of the coefficient of thermal diffusion to the coefficient of ordinary diffusion. It determines the amount of separation in any given case. Over a distance within which  $k_t$  may be regarded as constant, the resulting separation will be proportional

\* D. Enskog, *Phys. Zeit.* 12, 538 (1911); *Ann. d. Phys.* 38, 742 (1912). S. Chapman, *Proc. Roy. Soc. A*, 93, 1 (1916); *Phil. Trans. A*, 217, 157 (1917); *Phil. Mag.* 34, 146 (1917); 38, 182 (1919); 48, 602 (1924); *Proc. Roy. Soc. A*, 119, 34 (1928); 119, 55 (1928); *Phil. Mag.* 7, 1 (1929). Chapman and Dootson, *Phil. Mag.* 33, 268 (1917). T. L. Ibbs, with a note by S. Chapman, *Proc. Roy. Soc. A*, 99, 385 (1921); 107, 470 (1925). Ibbs and Underwood, *Proc. Phys. Soc.* 39, 227 (1927). Elliott and Masson, *Proc. Roy. Soc. A*, 108, 378 (1925).

to  $\log (T_1/T_2)$ ,  $T_1$  being the temperature of the hot side and  $T_2$  of the cold side. The value of  $k_t$  depends upon the masses and sizes of the molecules, and upon the proportions of the two gases in the mixture; it also depends upon the nature of the forces operating during collision, being a maximum for rigid elastic spheres, while it disappears entirely for molecules obeying an inverse fifth power law of repulsion.

In practice it is convenient to make measurements on thermal diffusion by observing the difference in composition in two vessels maintained at steady temperatures and joined by a connecting tube. The difference in percentage composition by volume of the gas in two such vessels will be termed the percentage separation. In a series of experiments\* made with a number of mixtures of different gases, one vessel being at a steady temperature of about  $15^\circ \text{C.}$  and the other at temperatures up to about  $300^\circ \text{C.}$ , it was found that for any given mixture the percentage separation was closely proportional to  $\log (T_1/T_2)$ , so that over this range  $k_t$  could be regarded as constant. (Elliott and Masson†, with a hot side at about  $500^\circ \text{C.}$ , obtained relatively greater separation for a number of gas mixtures). Any deviation from this proportionality was not greater than the possible error of the experiments. Thus for this range of temperatures the behaviour of the gases could be represented by molecules which are point centres of force obeying a constant inverse-power law of repulsion, although it is possible that the same behaviour might be represented by a more complicated molecular model.

At the time of publication of the results of an earlier series of experiments, Prof. Chapman suggested to one of us (T. L. I.) that it would be interesting to make experiments with one vessel at the temperature of liquid air. A preliminary experiment, made with the object of testing this suggestion for a mixture of hydrogen and nitrogen, showed that the amount of separation was relatively less than that obtained in experiments at higher temperatures. This apparent change in the value of  $k_t$  suggested the need for a more complete investigation to discover, if possible, the nature of the change and to find if it occurred in other gas mixtures also.

When experiments are made over an extended range of temperature, the separation produced by thermal diffusion may be considerable. The resulting variation in the proportions of the gases in different parts of the connecting tube will itself produce some variation in the value of  $k_t$ , and the possible effect of this fact must be considered when the results are examined.

## § 2. METHOD OF EXPERIMENT

In this work we have attempted to make a general study of the phenomenon at low temperatures rather than a close examination of any special pairs of gases. When the work was begun there was little to indicate which would be the most profitable gases to study. For the present purpose we simplified the experimental work by keeping as closely as possible to our original methods, and using con-

\* T. L. Ibbs, *loc. cit.* (1925).

† *Loc. cit.*



siderable quantities of gas. Further experiments are now in progress dealing with gases in smaller quantities; this work requires more manipulation, and progress is consequently slower.

We examined each gas mixture by keeping one side of the apparatus at practically constant temperature by means of a flow of water from the mains, and making measurements with the other side at a number of temperatures down to

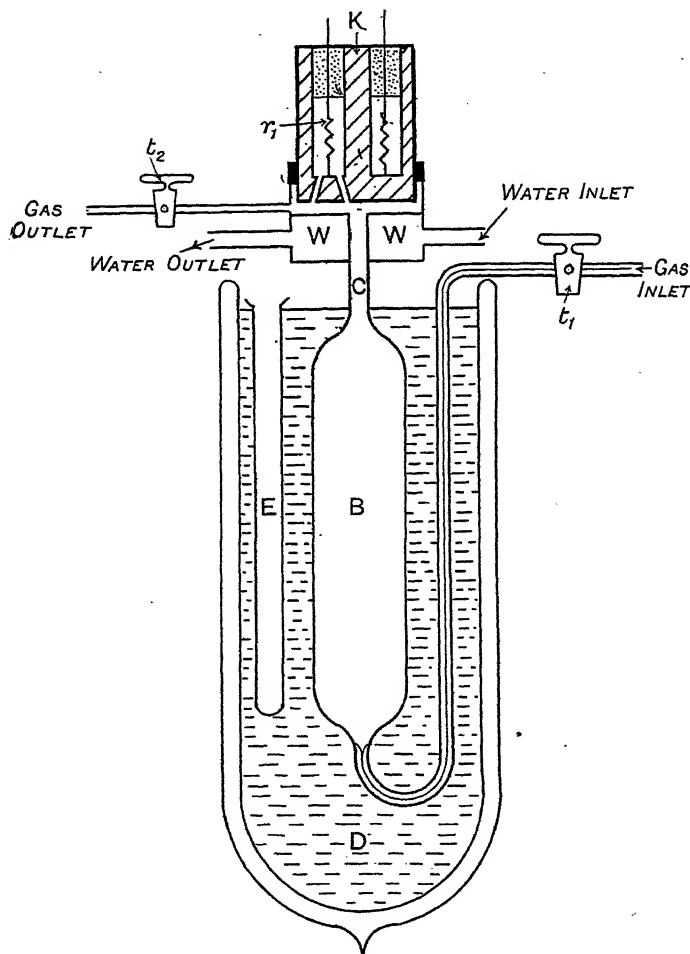


Fig. 1. Diagram of apparatus.

that of liquid air, or down to the point where one of the constituents liquefied. The principle of the experiment was similar to that previously adopted, with one large and one small vessel joined by a connecting tube. With this arrangement practically the whole effect of thermal diffusion can be made to appear as a change in composition of the gas in the smaller vessel. A diagram of the apparatus is shown in Fig. 1. The katharometer\* was again used, but it was convenient in this

\* This instrument was kindly lent by Dr G. A. Shakespear.

case to put the katharometer block *K* at the top; this block is kept at constant temperature by means of the water jacket *W*. The exposed cell *r* and its connections, with a total volume of 1.0 c.c., form what must now be regarded as the small hot side, all at the temperature of the water jacket. The hot side is joined by means of a connecting tube *C* of length about 3 cm. and internal diameter 0.4 cm. to the glass bulb *B*, of volume 45.0 c.c., which forms the large cold side. The bulb *B* was cooled by means of a surrounding Dewar vessel *D*, generally containing a cooling liquid such as liquid air or cold pentane. This arrangement of the apparatus, with the cold side below, avoids errors which might arise owing to convection and also enables the cooling liquid to be applied without difficulty. By a rapid flow of water maintained through *W* the katharometer was effectively screened from the cooling effect of the liquid in the Dewar vessel.

The gas mixture to be examined was made in a cylinder under pressure, and sufficient time was allowed for it to attain uniformity of composition. The Dewar vessel containing a cooling liquid was put in position, and the apparatus was flushed out, the gas mixture entering at tap *t*<sub>1</sub>, passing through the glass capillary tube to the cold bulb *B*, through the connecting tube *C*, past the katharometer block, and out at the tap *t*<sub>2</sub>. The method was again adopted of allowing the gas to pass sufficiently quickly through the connecting tube to overcome the effect of thermal diffusion, so that the whole apparatus was filled initially with a mixture of uniform composition. The flow was then stopped, the taps were closed, and the resulting change in composition on the hot side was measured by means of the katharometer. The corresponding change in composition of the gas in the glass bulb of the cold side can be calculated; this change depends upon the relative volumes of the hot and cold sides, and upon their temperatures. With the present arrangement the change on the cold side is small, being only about 0.006 of the change on the hot side, when the bulb *B* is in liquid air.

The electrical arrangements of the katharometer were similar to those previously employed, and the general use of the instrument was the same as before.

*Method of cooling.* Many preliminary experiments were made in order to develop a suitable method of cooling the glass bulb to a number of temperatures, down to that of liquid air. In the early experiments freezing mixtures were used, such as ice and sodium chloride. Carbon dioxide snow was also used either alone or mixed with methylated spirits. Although these methods presented practical difficulties in obtaining uniform temperatures, the thermal diffusion effect was clearly shown. A typical set of results for a mixture of hydrogen and nitrogen is given in Fig. 2. It will be seen that the separation is proportional to  $\log(T_1/T_2)$  down to the point given by carbon dioxide snow, and that if the straight line is produced, the point corresponding to the separation and temperature produced by liquid air lies considerably below it. This fact indicated the need for using a number of temperatures below that of carbon dioxide snow, more especially as few ordinary gases can be taken to the liquid air temperature without liquefaction occurring. Pentane was finally adopted as the cooling liquid. This was generally cooled in the Dewar vessel before it was placed round the bulb *B*. A large test-tube was

placed in the pentane, and liquid air poured into it, causing the pentane to cool rapidly. The Dewar vessel was then placed round the bulb. For the lower temperatures it was necessary to cool the pentane further, when the Dewar vessel was in position. In this case a small tube *E* was put into the pentane (Fig. 1), and a quantity of liquid air injected into it, so as to cause a further fall in temperature of the bulb *B*. (The liquid air required for this purpose was kept in a second Dewar vessel, fitted with a cork, mouthpiece, and delivery tube, and it was blown

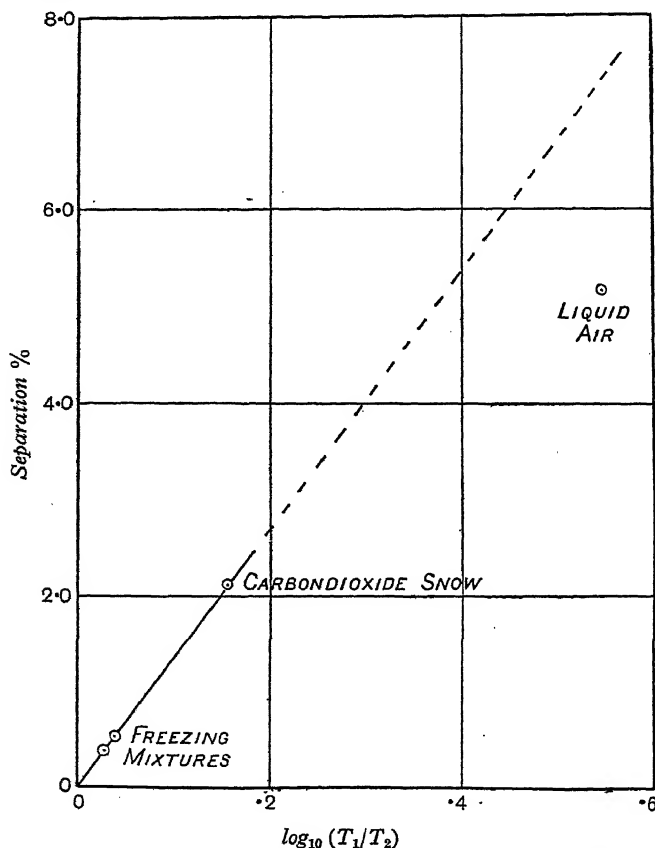


Fig. 2. Preliminary experiments (35.8 %  $H_2$ , 64.2 %  $N_2$ ).

over as required into the tube *E*.) In this way the temperature of the bulb could be controlled to some extent, and a mixture of gases could be cooled until one constituent liquefied. This method of controlling low temperatures is somewhat similar to that described by Patterson\*.

It was necessary to stir the pentane to keep the whole of the bulb *B* at practically the same temperature. Several different methods of stirring were tried, and the method finally adopted was to bubble compressed air from a cylinder through the liquid. This was found to be more effective than the use of a mechanical stirrer, and it did not cause any serious rise in temperature of the contents of the Dewar

\* W. H. Patterson, *Phil. Mag.* 2, 383 (1926).

vessel. At  $-125^{\circ}\text{C}$ . the rise in temperature was about half a degree per minute, which did not produce any difficulty in making the observations. Using the method described, we were able to obtain temperatures down to about  $-140^{\circ}\text{C}$ .; as the pentane solidified at about  $-150^{\circ}\text{C}$ .

As we experienced difficulty in obtaining supplies of pentane of lower freezing point, it was necessary to devise a method of obtaining temperatures between  $-140^{\circ}\text{C}$ . and  $-190^{\circ}\text{C}$ . The use of a liquid as a cooling medium had to be abandoned, and the following method was substituted. The same Dewar vessel was used, and a quantity of cotton wool was placed at the bottom. A piece of thin copper sheet was bent into the form of a tube lining the inner walls of the vessel, and resting on the cotton wool. The vessel was filled with liquid air and then emptied, except for the small quantity remaining absorbed in the cotton wool. It was then placed in position round the bulb *B*, which had previously been immersed for a short time in liquid air, and the mouth of the Dewar vessel was plugged tightly with cotton wool. In this way we found that a minimum temperature, of about  $-170^{\circ}\text{C}$ . at the middle of the bulb, could be obtained. This would remain steady for 15 minutes or longer, depending on the quantity of liquid air in the wool. The temperature then began to rise, slowly at first, and then more rapidly. Thermal diffusion measurements were made during the steady period, and the initial parts of the rise. As heat enters the vessel from its mouth, it was not possible in the use of this method to avoid a fairly uniform temperature gradient throughout the length of the bulb. With the middle of the bulb at  $-170^{\circ}\text{C}$ . there was a temperature difference of about  $20^{\circ}$  between its ends: this temperature gradient will produce some thermal diffusion in the bulb itself. Simple considerations of the thermal diffusion effect show that with the present arrangement of a small hot side and a large cold side, we introduce little error by regarding the temperature at the middle as the temperature of the bulb, and measuring the change in composition on the hot side as before. Measurements made in this way at rather higher temperatures were found to be in satisfactory agreement with those obtained by the use of pentane, and the portion of the curves obtained by this method terminated smoothly in the point obtained by the use of liquid air.

In mixtures containing hydrogen the thermal separation was practically complete in about five minutes, but it was observed that the rate at which the effect took place tended to be less at the lower temperatures.

*The temperature measurements.* The cold side temperatures were measured down to  $-120^{\circ}\text{C}$ . with a toluol thermometer graduated in degrees. For lower temperatures a pentane thermometer, also marked in degrees, was used. The thermometers were normally supported in the Dewar vessel with the bulb near the middle of the glass bulb *B*. A constant volume hydrogen thermometer was made and was used to check the accuracy of the thermometer readings. The toluol thermometer was found to be correct to within a degree over its entire range. The error of the pentane thermometer was greater and was variable, but not sufficiently to have any serious effect on our results. The simplicity gained by the use of this thermometer was an important point in its favour.

The temperature of liquid air was measured by the hydrogen thermometer and was found to be  $-192^{\circ}\text{C.}$  after the liquid air had been standing for two or three hours; it was convenient to adopt this in a number of cases as the liquid air temperature.

A thermo-couple was used for some of the temperature measurements; it was calibrated by means of the hydrogen thermometer.

The hot side temperature was measured by means of an ordinary mercury thermometer placed in the water, where it issued from the water jacket.

*Miscellaneous details.* The measurements were generally made at atmospheric pressure. Pressures can therefore be regarded as atmospheric, unless otherwise shown. The process of flushing out with the gas was repeated for each measurement.

The gases used were taken from cylinders. To prevent errors due to the condensation of water vapour or other easily liquefied impurities, the gas mixtures were passed through a U-tube immersed in liquid air or cooled pentane, before entering the apparatus. In this way such impurities could be removed. Small amounts of other impurities would have no serious effect on the results.

Most of the mixtures now used had previously been examined at higher temperatures, and it was convenient to use the old katharometer calibration curves which had been obtained on another instrument. This procedure will not affect the general nature of the results, and it should not cause any serious error in the absolute amounts of separation now recorded. The initial portions of the curves given by these low-temperature experiments yield values of  $k_i$  which are in reasonable agreement with values obtained from our previous higher-temperature experiments. This is evidence for the consistency of the method of measurement. Minor differences occasionally occur: for example, the values of  $k_i$  for mixtures of hydrogen and nitrous oxide are lower than previously recorded. There is little doubt that in due course we shall be able to adjust any such irregularities.

### § 3. EXPERIMENTAL RESULTS

Eight pairs of gases were examined. It is convenient to divide the experiments into three groups for the consideration of results.

Group 1. Measurements on mixtures of (a) hydrogen and carbon dioxide; (b) hydrogen and nitrous oxide; (c) hydrogen and ethylene.

Group 2. Measurements on mixtures of (a) hydrogen and nitrogen; (b) hydrogen and carbon monoxide; (c) hydrogen and oxygen; (d) hydrogen and argon.

Group 3. Measurements on mixtures of nitrogen and argon.

Each pair of gases was examined in mixtures of three or more different proportions. Each mixture was examined with the cold side at about eight different temperatures, ranging from about  $-30^{\circ}\text{C.}$  to  $-192^{\circ}\text{C.}$ , or to the liquefaction point of one of the constituents if this was above  $-192^{\circ}\text{C.}$  In a series of measurements on a given mixture, the temperature  $T_1$  of the hot side rarely varied by more than  $1^{\circ}\text{C.}$ , so that the values of  $\log(T_1/T_2)$  can be regarded as referring to

definite hot and cold side temperatures. For different mixtures, the hot side temperature may differ rather more widely, as shown in the tables.

As the primary object of these experiments is to investigate the variation of thermal separation with temperature, curves have been plotted showing the relation between separations as ordinates and  $\log_{10} (T_1/T_2)$  as abscissae. The value of  $k_t$  determines the slope of these curves since, over a given distance  $dx$ ,

$$k_t = -d\lambda_1/d(\log T).$$

With the present arrangement, where the hot side temperature can be regarded as constant for any given mixture, the slope of the curve at any point is proportional to the value of  $k_t$  in a region where the temperature is  $T_2$ , i.e. the cold side temperature corresponding to the point. Hence numerical values of  $k_t$  can be obtained, if required, from the slope of the curves.

It will be found that the first portion of the curve is in all cases a straight line, so that  $k_t$  can be regarded as constant over a considerable temperature range. The changes in slope which occur in many cases at the lower temperatures indicate a gradual fall in the value of  $k_t$  as  $T_2$  is reduced. In no case does the value of  $k_t$  appear to increase as the temperature is lowered.

The differences in slope of the curves shown for different mixtures of any given pair (see, for example, Fig. 3) are due, of course, to the different proportions of the two gases in the mixtures. This dependence of  $k_t$  on the proportions of the gases in the mixture has already been investigated experimentally, and the results are in agreement with the theoretical prediction.

With our present arrangement of a small hot and a large cold side, the separating effect of thermal diffusion will cause the proportion of the lighter gas to increase, from the cold end to the hot end of the connecting tube. Most of the mixtures we have now examined have been arranged to contain less than 50 per cent. of the lighter gas, which was generally hydrogen: this means that the separating effect in the connecting tube will on the whole tend to cause a small apparent increase in the value of  $k_t$  as  $T_2$  is reduced. The change is small, but it appeared desirable to make it opposite in sign to the interesting falling off in the value of  $k_t$  which we have observed at lower temperatures.

*Group 1. Hydrogen and (a) carbon dioxide; (b) nitrous oxide; (c) ethylene.* For all these pairs, one of the constituents liquefies at a temperature above that of liquid air. Measurements could be made in these cases down to within about  $1^\circ$  of the liquefaction point by cooling the pentane when in position round the bulb, as described. If liquefaction occurred in the cold bulb, it was immediately indicated by the katharometer's showing a sudden increase in the proportion of hydrogen.

Fig. 3 shows the results for three mixtures of hydrogen and carbon dioxide. It will be seen that the separation is closely proportional to  $\log (T_1/T_2)$  even when the liquefaction point of the carbon dioxide is approached. This proportionality at the low temperatures is striking, and means that  $k_t$  is constant over this range of temperature. If there were any serious change from the ordinary gas conditions at the lower temperatures, we should expect some deviation to be shown.

Clustering of the molecules would probably affect the thermal diffusion and thus produce a change in the value of  $k_t$ , or it would produce a partial separation in the mixture, with a consequent alteration in the proportions on the two sides, quite apart from the effect of thermal diffusion. All these mixtures behaved in the same way. The constant value of  $k_t$  in these cases, as the liquefaction point is approached, is of special interest when we come to consider the results of other mixtures.

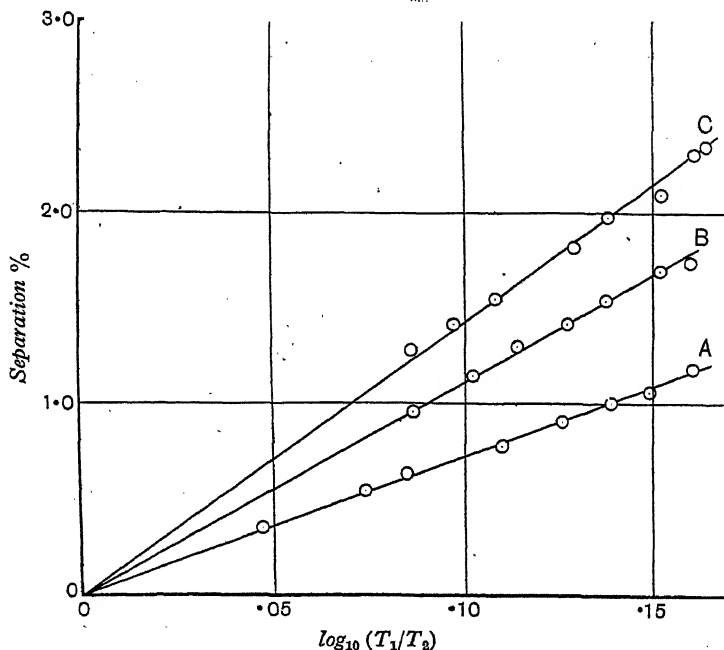


Fig. 3. H<sub>2</sub>-CO<sub>2</sub> mixtures. A, 18.4 % H<sub>2</sub>; B, 34.0 % H<sub>2</sub>; C, 45.2 % H<sub>2</sub>.

The results for hydrogen and nitrous oxide are similar to those for hydrogen and carbon dioxide and are shown in Table 5. The liquefaction point of ethylene ( $-102^{\circ}\text{C.}$ ) is somewhat lower than that of carbon dioxide, but proportionality is still observed. Measurements were made at temperatures down to  $-98^{\circ}\text{C.}$  (see Fig. 4).

*Group 2. (a) Hydrogen and nitrogen.* Low temperature measurements on mixtures of this pair can be made over a wide range, the cold side being taken down to the temperature of liquid air, i.e. to within a few degrees of the liquefaction point of nitrogen. Preliminary experiments on this pair had already shown that the separation produced when the cold side is at liquid-air temperature is proportionally less than the normal amount. By means of the methods described, complete curves could now be obtained down to the liquid-air point, as shown in Fig. 5 for two mixtures. They show that the separation is proportional to  $\log (T_1/T_2)$  until the cold side reaches about  $-100^{\circ}\text{C.}$  At lower temperatures the proportionality no longer holds, the separation falling below its ordinary value, until at  $-190^{\circ}\text{C.}$ ,

the total separation is about 20 per cent. less than normal. This falling off in the effect begins at temperatures which can be attained by the method of cooling with pentane. The amount by which the observed separation falls below the normal value is approximately the same for all the mixtures, as is also the temperature at which the departure from the normal value begins.

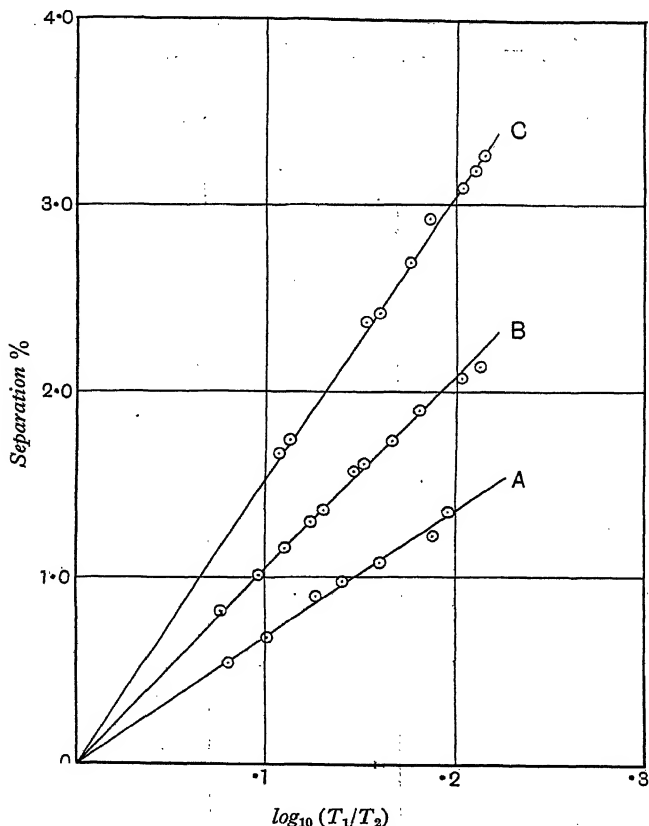


Fig. 4. Mixtures of  $H_2-C_2H_4$ . A, 16.5 %  $H_2$ ; B, 28.0 %  $H_2$ ; C, 58.5 %  $H_2$ .

*Group 2. (b) Hydrogen and carbon monoxide.* The low liquefaction point of carbon monoxide makes it a suitable gas for low-temperature investigation. It is of interest also to compare the behaviour of mixtures of this pair of gases, with that of mixtures of hydrogen and nitrogen. We again find that the behaviour of the two pairs is similar. Below about  $-100^\circ C$ . the separation is no longer proportional to  $\log (T_1/T_2)$ . At  $-192^\circ C$ . the observed value is again about 20 per cent. below the normal or proportional value. The results are shown in Table 8.

*Group 2. (c) Hydrogen and oxygen.* These are the first measurements which we have made on this pair of gases. The mixture which was examined showed the falling off in the effect at low temperatures; the behaviour of oxygen with hydrogen



being very similar to that of nitrogen with hydrogen. The results are shown in Table 10.

*Group 2. (d) Hydrogen and argon.* The preceding experiments have shown that for mixtures of certain diatomic gases with hydrogen, the proportionality between the separation and  $\log(T_1/T_2)$  does not hold at low temperatures. In the present case argon is substituted for the diatomic gas. Argon was chosen because it is available in sufficient quantities for this method of experiment and has a suitably low liquefaction point,  $-186^\circ\text{C}$ ., although measurements cannot be made at

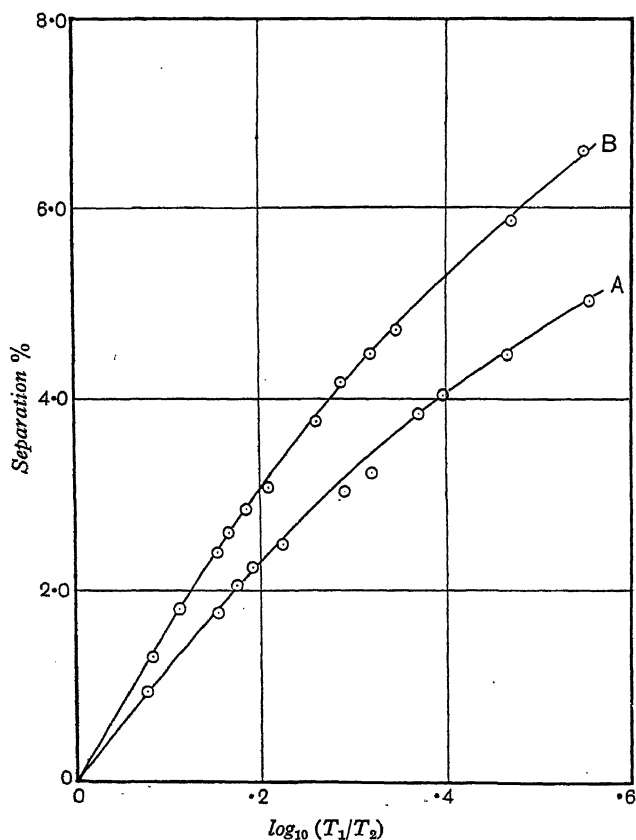


Fig. 5. Mixtures of  $\text{H}_2\text{-N}_2$ . A, 29.4 %  $\text{H}_2$ ; B, 42.0 %  $\text{H}_2$ .

atmospheric pressure with the use of liquid air. The curves obtained are similar to those given by the previous mixtures in this group, see Fig. 6. At  $-170^\circ\text{C}$ . the observed separation is about 16 per cent. below the proportional value. The cold side temperature at which the proportionality begins to fail is about  $-80^\circ\text{C}$ ., and it thus appears to be definitely higher than in the cases already considered.

*Group 3. Nitrogen and argon.* All mixtures previously examined in this work have contained hydrogen, so that measurements could be taken down to the liquefaction point of the other constituent. The lightness of the hydrogen molecule

also enables a considerable separation to be obtained and so assists the accuracy of the measurements.

However unlikely it may appear, there was a possibility that the falling off in the value of  $k_t$  at low temperatures might have been due to some unique property of hydrogen. It was desirable therefore to find a pair of gases, not containing hydrogen, which could be examined at low temperatures. Nitrogen and argon mixtures were suited to our purpose, as both gases are available in suitable quantities. Three different mixtures were examined.

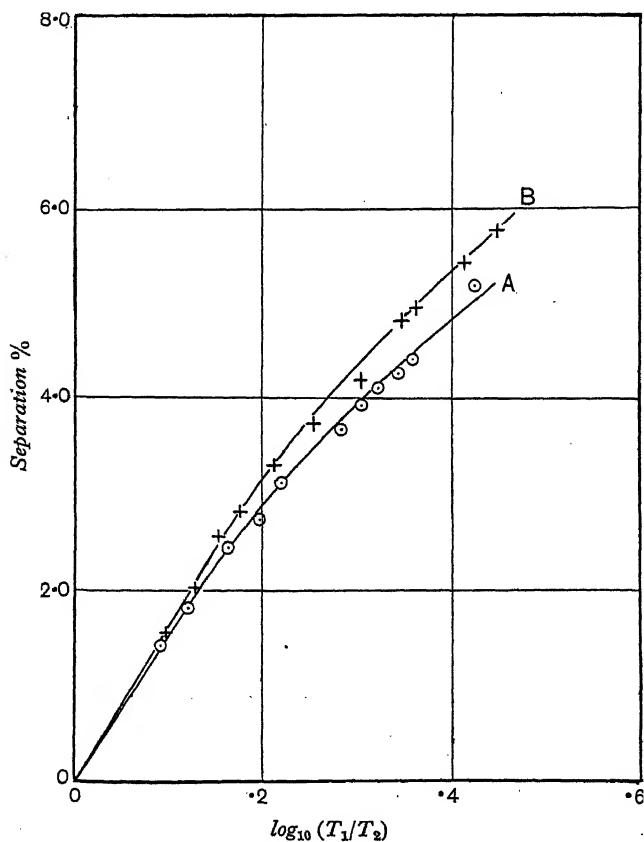


Fig. 6. Mixtures of  $H_2$ -A. A, 47.0 %  $H_2$ ; B, 55.6 %  $H_2$ .

The actual amount of separation was less than before, because the masses of the molecules are more alike. The measurements cannot therefore be made with the same degree of accuracy. The time taken to reach the steady state was much longer than for hydrogen mixtures.

The results for two mixtures are shown in Fig. 7. It will be seen from the curves that the falling off in the value of  $k_t$  is much more pronounced than in any previous case. The observed separation at  $-170^\circ C.$  is about 40 per cent. below the ordinary proportional value, or about twice the reduction shown in the hydrogen

mixtures of Group 2. This fact suggests that the deviation may be due not to the hydrogen molecules, but rather to the nitrogen, argon or other molecules in the mixtures.

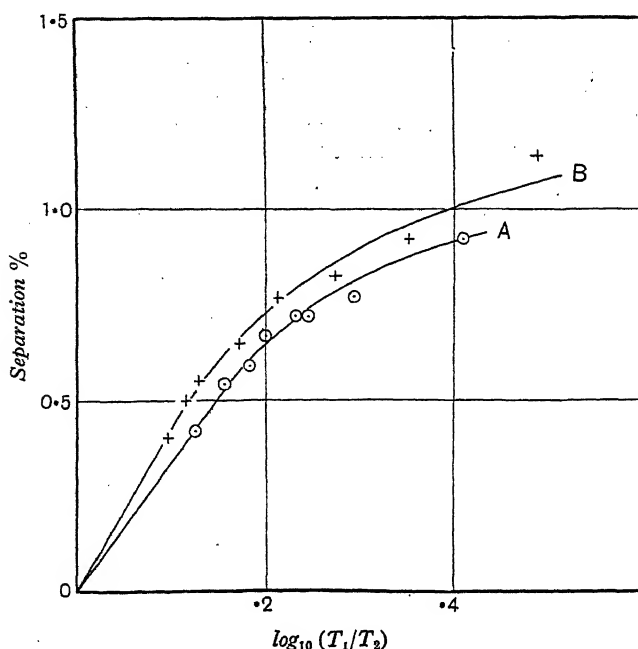


Fig. 7. Mixtures of N<sub>2</sub>-A, 70.0 % N<sub>2</sub>; B, 46.0 % N<sub>2</sub>.

#### § 4. MEASUREMENTS OF THERMAL DIFFUSION MADE UNDER VARYING GAS PRESSURES

The question arises, whether the nature of our results at the low temperatures is due to a departure from the simple gas conditions postulated in the theory. Experiments made on the variation of the viscosity of gases with temperature show that the behaviour is not normal at the lower temperatures. Thus, a number of observers\* have shown that the observed values of the coefficient of viscosity at low temperatures is greater than that predicted by Sutherland's law. Various attempts have been made to explain this effect as due to clustering of the molecules, multiple encounters or other causes. Reference will be made later to the work of Lennard-Jones, who regards the ordinary gas conditions as still holding.

In our case, the measurements of Group 1 have already suggested that the gas conditions which are generally postulated in the kinetic theory can be regarded as holding until one of the constituents liquefies. This suggests that the behaviour of the mixtures in Groups 2 and 3 is not due to a departure from the simple gas conditions, although the temperatures used are now lower. A further test of the persistence of the simple gas conditions may be applied by means of measure-

\* For references see S. Chapman, *Phil. Trans. A*, 216, 342 (1916).

ments of thermal diffusion made under different gas pressures. By reducing the pressure, we may expect to reduce the possibility of molecular aggregation or multiple encounters.

For these experiments the flow method, which had previously been used, was discontinued. The apparatus was first filled with a mixture at atmospheric pressure, the large glass bulb *B* being at the temperature of the room, and both taps closed. The cooling liquid was then placed round the glass bulb, causing thermal diffusion to take place, and also reducing the pressure of the gas inside the apparatus. The

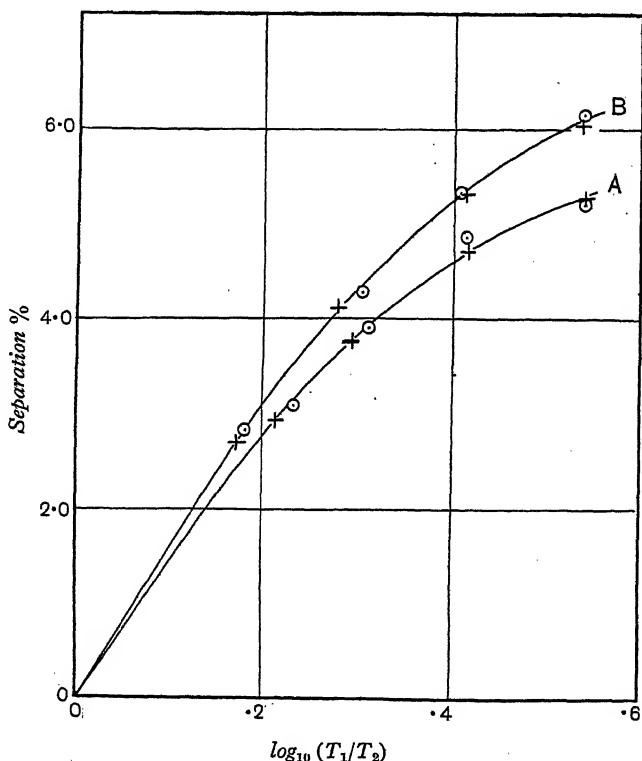


Fig. 8. Experiments with varying pressure. +, atmospheric pressure; ⊙, reduced pressure; A, 36.0 % H<sub>2</sub>, 64.0 % CO; B, 43.5 % H<sub>2</sub>, 56.5 % N<sub>2</sub>.

extent to which the pressure was reduced depended of course upon the temperature of the cooling liquid. When liquid air was used the pressure inside the apparatus was reduced to about 0.27 of the initial pressure.

The reduction of pressure inside the apparatus will itself affect the katharometer readings, the change in readings for any given pressure depending upon the gas mixture used. The necessary correction for this effect can be made by means of a separate experiment, in which the apparatus is first filled with the gas mixture at atmospheric pressure. The pressure is then reduced by means of a pump, and the effect of the change in pressure on the readings of the galvanometer is directly observed. In this way a curve can be plotted for any given mixture, showing the

effect of change of pressure on the readings, and by reference to this curve the necessary correction can easily be made.

Thermal diffusion measurements were thus made under reduced pressure on mixtures of hydrogen and nitrogen and of hydrogen and carbon monoxide. Measurements were also made on the same mixtures in the usual way at atmospheric pressure. In this way it was found that the two sets of measurements gave practically identical results. In Fig. 8 it will be seen that the falling off in the effect at low temperatures is the same for both methods of measurement. This fact appears to afford satisfactory evidence of the simplicity of the gas conditions. The evidence is supported by the work of Dewar\* who concludes "that either a simple or compound gas, at an initial pressure somewhat less than one atmosphere, may be relied on to determine temperatures down to its own boiling point, in the constant volume gas thermometer." We are therefore justified in not attributing the peculiarities of thermal diffusion at low temperatures to a failure in the gas conditions.

Apart from their value for this special purpose, the results of these experiments made under varying pressures supply additional confirmation of the general theory. All our measurements have previously been made at atmospheric pressure. The theory shows that the effect depends upon the proportions of the gases in a mixture, and not upon the molecular density of the constituents. The value of  $k_t$  will therefore be independent of the pressure of the gas. This prediction is now confirmed experimentally. A more detailed study of thermal diffusion over an extended range of pressures would be interesting.

## § 5. DISCUSSION OF RESULTS

Experiments on the variation of viscosity with temperature have shown that, over a limited range of temperature, the molecules of gases can be represented as point centres of repulsive force obeying an inverse power law†. This discovery provided the first information on the nature of inter-molecular forces in gases. The behaviour of viscosity over an extended range of temperature cannot generally be explained by means of molecules of this type, and Sutherland's model, which allows for the attractive forces between molecules, in some cases gives better agreement. In thermal diffusion we are dealing with the forces between molecules of different kinds, but the behaviour in collisions will probably be of a similar general character to that in collisions between the molecules of a simple gas.

The constant value of  $k_t$  which we have observed over a limited range of temperature for all pairs of gases suggests that the molecules might again be regarded as point centres of repulsive force. The falling off in the value of  $k_t$  at the lower temperatures might be due to a change in the nature of the collisions as the temperature is reduced. If we regard molecules simply as point centres of repulsive force, then we must consider them to become softer as the temperature falls, i.e.

\* Dewar, *Proc. Roy. Soc.* 68, 49 (1901).

† Cf. Jeans, *Dynamical Theory of Gases*, 3rd edition, para. 380.

the index of the power law is reduced. A better representation of real molecules appears to be given by regarding them as point centres of both attractive and repulsive force. This model has been used very successfully by Lennard-Jones\* in a number of cases. For example, a close representation of the viscosity of argon can be obtained over the entire range of temperature for which it has been observed. The theory of thermal diffusion, which at present deals with molecules as point centres of repulsion only, is highly complex. Chapman has shown that there is little prospect of developing a simple physical theory like those applied to many of the phenomena considered by the kinetic theory, and any attempt to extend the theory to include the effects of attractive forces will no doubt further increase its complexity. The general nature of our experimental results suggests, however, that the decrease in the value of  $k_t$  at the lower temperatures may be due to the effect of these attractive forces. As the temperature is reduced the molecules penetrate less deeply into the fields of force during an encounter. The attractive forces of the van der Waals' type become relatively more important than the repulsive forces with increasing distance; and it seems possible that the effect of this circumstance on the nature of the collisions may be equivalent to a softening of the molecules at the lower temperatures. Definite conclusions on this question can only be reached with the aid of a complete theoretical investigation. It appears unlikely that the observed behaviour of thermal diffusion at low temperatures can be due directly to the effective change in the sizes of the molecules.

The range of temperature in which the gases of Group 1 can be examined does not extend below about  $-100^\circ\text{C.}$ , and the value of  $k_t$  is practically constant in that group. This does not necessarily mean that repulsive forces only are operating during an encounter. The superposed attractive and repulsive fields may produce the effect of a repulsive field, with power law of lower index. More exact experiments may show that there is a definite variation in  $k_t$  over this range, but it is probable that any such variation will be very small.

For Group 2  $k_t$  can again be regarded as constant over a considerable range, after which it decreases with temperature. It is interesting to compare the experimental value of  $k_t$  obtained at different temperatures for a mixture of hydrogen and nitrogen with the theoretical value for rigid elastic spheres. Using Chapman's formulae† with numerical values inserted for hydrogen-nitrogen mixtures, we obtain

$$k_t = \frac{5}{2} \left[ \frac{0.220\lambda_1 + 0.195\lambda_2}{1.784 + 1.430\lambda_1/\lambda_2 + 0.438\lambda_2/\lambda_1} \right].$$

Applying this, we find that  $k_t = 0.0984$  for rigid elastic spheres, corresponding to a mixture containing 29.4 per cent. of hydrogen. From the slope of the curve shown in Fig. 5 we obtain the experimental values of  $k_t$  for different temperatures of the cold side  $T_2$ . These values are shown in Table 1.

\* Lennard-Jones, *Proc. Roy. Soc. A*, 106, 441 (1924); 107, 157, 636 (1925); 109, 584 (1925); 112, 214 (1926); 115, 334 (1927).

† *Phil. Mag.* 48, 602 (1924).

Table 1

$T_2$	0° C.	- 50° C.	- 100° C.	- 150° C.	- 190° C.
$k_t$ experimental	0.050	0.050	0.043	0.032	0.025
$\frac{k_t \text{ experimental}}{k_t \text{ rigid elastic spheres}}$	0.51	0.51	0.435	0.315	0.255

Thus the experimental value of  $k_t$  at  $-190^\circ$  C. is about half the value obtained at ordinary temperatures. Other curves for mixtures of these gases yield similar results. The curves for other gas mixtures can be dealt with in the same way.

The measurements on mixtures of hydrogen and oxygen are the first which we have made on this pair of gases. It is interesting to observe that the general behaviour of the pair, which combine chemically, is similar to that of hydrogen and argon. Thus chemical affinity does not appear to have any direct bearing on the thermal diffusion effect, and this fact suggests that such affinity does not influence the nature of the forces arising between molecules during collisions. The similarity mentioned above applies to the general amount of separation, and to the falling off at lower temperatures. Experiments made by Masson and Dolley\* on the compressibilities of mixtures of ethylene and oxygen, and of ethylene and argon, showed that the behaviour of the two mixtures was practically the same. They therefore conclude that the van der Waals' attraction between the molecules of different gases in a mixture does not arise from chemical affinity. Our observations showing that chemical affinity does not appear to have any direct influence on the thermal diffusion effect afford general support to such a conclusion. Chemical forces and cohesive forces may both be of electronic origin, but there is probably a fundamental difference in their nature. We hope in due course to make further experiments dealing with this aspect of the subject.

For oxygen-hydrogen mixtures Chapman and Hainsworth give

$$k_t = \frac{5}{2} \left\{ \frac{0.204\lambda_1 + 0.177\lambda_2}{1.630 + 1.320\lambda_1/\lambda_2 + 0.405\lambda_2/\lambda_1} \right\}.$$

Applying this formula to a mixture containing 29.8 per cent. of hydrogen, we find that  $k_t = 0.100$ . Comparing this with experimental values, by using a curve as before, we obtain the results shown in Table 2.

Table 2

$T_2$	0° C.	- 50° C.	- 100° C.	- 150° C.	- 180° C.
$k_t$ experimental	0.048	0.048	0.043	0.024	0.020
$\frac{k_t \text{ experimental}}{k_t \text{ rigid elastic spheres}}$	0.48	0.48	0.43	0.24	0.20

\* Masson and Dolley, *Proc. Roy. Soc. A*, 103, 524 (1923).

For mixtures of nitrogen and argon the variation of  $k_t$  with temperature is greater. As before, we obtain the general formula for  $k_t$  for rigid elastic spheres corresponding to nitrogen-argon mixtures. Thus

$$k_t = \frac{5}{2} \left\{ \frac{0.100\lambda_1 + 0.116\lambda_2}{3.693 + 1.748\lambda_1/\lambda_2 + 1.889\lambda_2/\lambda_1} \right\}.$$

Applying this to a mixture of 30 per cent. argon, we find that  $k_t = 0.0314$ . From the slope of the curve shown in Fig. 7 we again obtain experimental values of  $k_t$  in regions corresponding to different temperatures of the cold side  $T_2$ . These values are shown in Table 3.

Table 3

$T_2$	0° C.	- 50° C.	- 100° C.	- 150° C.	- 180° C.
$k_t$ experimental	0.0148	0.0148	0.0075	0.0036	0.0016
$\frac{k_t \text{ experimental}}{k_t \text{ rigid elastic spheres}}$	0.472	0.472	0.239	0.114	0.051

Measurements of the viscosity of hydrogen at low temperatures show that Sutherland's law is not followed. Better representation of the experimental results is given by regarding the molecules as point centres of repulsive force\*. This means that for hydrogen the attractive forces are weak; thus in mixtures of nitrogen and argon we may expect the attractive forces between unlike molecules to be greater than in mixtures with hydrogen as one constituent. The great variation with temperature in the experimental value of  $k_t$  for nitrogen-argon mixtures gives support to this view.

It is interesting therefore to consider the possibility of obtaining a pair of gases for which the value of  $k_t$  will remain constant down to - 190° C., or for which its variation with temperature will be small. Lennard-Jones has shown that the attractive forces for both helium and neon are weak. We may therefore expect that in mixtures of helium and neon or hydrogen and neon the influence of the attractive forces will be small. Experiments dealing with these two pairs of gases and with other mixtures containing inert gases are now in progress. For this extension of the work considerable modification of the apparatus and method is required.

Tables showing the results of a final series of measurements have been included in the paper so that they may be available if required for the purpose of calculation.

## § 6. ACKNOWLEDGMENT

In conclusion, we desire to express our thanks to Prof. S. W. J. Smith, who has granted full facilities for this work.

\* Cf. Jeans, *Dynamical Theory of Gases*, p. 286.



Table 4. Hydrogen and carbon dioxide

$18.4\% \text{ H}_2$ $T_1 = 11^\circ \text{C.}$			$34.0\% \text{ H}_2$ $T_1 = 12^\circ \text{C.}$			$45.2\% \text{ H}_2$ $T_1 = 13^\circ \text{C.}$		
$T_2^\circ \text{C.}$	$\log_{10} (T_1/T_2)$	Separation %	$T_2^\circ \text{C.}$	$\log_{10} (T_1/T_2)$	Separation %	$T_2^\circ \text{C.}$	$\log_{10} (T_1/T_2)$	Separation %
-76.2	.161	1.18	-76.1	.160	1.74	-76.4	.164	2.34
-71.1	.149	1.06	-72.0	.152	1.69	-75.5	.161	2.30
-66.9	.139	1.00	-65.1	.137	1.53	-71.1	.152	2.09
-60.5	.126	0.91	-60.0	.127	1.42	-65.2	.138	1.97
-52.2	.110	0.78	-53.9	.114	1.29	-60.5	.129	1.82
-39.4	.085	0.63	-47.8	.102	1.14	-49.8	.108	1.55
-33.6	.074	0.54	-39.5	.087	0.96	-43.9	.097	1.41
-17.0	.047	0.34				-38.0	.086	1.28

Table 5. Hydrogen and nitrous oxide

$35.0\% \text{ H}_2$ $T_1 = 15^\circ \text{C.}$			$42.5\% \text{ H}_2$ $T_1 = 13^\circ \text{C.}$			$59.0\% \text{ H}_2$ $T_1 = 14^\circ \text{C.}$		
$T_2^\circ \text{C.}$	$\log_{10} (T_1/T_2)$	Separation %	$T_2^\circ \text{C.}$	$\log_{10} (T_1/T_2)$	Separation %	$T_2^\circ \text{C.}$	$\log_{10} (T_1/T_2)$	Separation %
-78.2	.169	1.68	-85.5	.183	2.02	-86.0	.186	2.31
-66.0	.143	1.43	-80.0	.170	1.87	-74.3	.161	2.03
-53.0	.117	1.18	-74.8	.161	1.81	-65.5	.141	1.81
-44.5	.100	0.98	-59.5	.126	1.49	-53.0	.116	1.47
-29.0	.071	0.72	-42.9	.094	1.08	-39.0	.089	1.13
			-37.8	.085	0.98			
			-30.2	.072	0.84			

Table 6. Hydrogen and ethylene

$17.0\% \text{ H}_2$ $T_1 = 15^\circ \text{C.}$			$28.0\% \text{ H}_2$ $T_1 = 14^\circ \text{C.}$			$58.5\% \text{ H}_2$ $T_1 = 14^\circ \text{C.}$		
$T_2^\circ \text{C.}$	$\log_{10} (T_1/T_2)$	Separation %	$T_2^\circ \text{C.}$	$\log_{10} (T_1/T_2)$	Separation %	$T_2^\circ \text{C.}$	$\log_{10} (T_1/T_2)$	Separation %
-89.8	.196	1.35	-97.5	.213	2.14	-98.1	.215	3.27
-85.9	.187	1.23	-92.8	.201	2.07	-93.2	.203	3.10
-74.0	.160	1.08	-84.0	.181	1.90	-97.3	.211	3.19
-65.3	.141	0.99	-71.4	.152	1.61	-81.4	.175	2.70
-58.3	.127	0.90	-60.2	.130	1.36	-71.8	.153	2.38
-44.8	.101	0.68	-50.5	.110	1.15	-50.8	.112	1.74
-33.7	.080	0.54	-31.4	.095	0.82	-47.9	.107	1.66

Table 7. Hydrogen and nitrogen

$29.4\% \text{ H}_2$ $T_1 = 16^\circ \text{C.}$			$42.0\% \text{ H}_2$ $T_1 = 16^\circ \text{C.}$			$77.5\% \text{ H}_2$ $T_1 = 15^\circ \text{C.}$		
$T_2^\circ \text{C.}$	$\log_{10} (T_1/T_2)$	Separation %	$T_2^\circ \text{C.}$	$\log_{10} (T_1/T_2)$	Separation %	$T_2^\circ \text{C.}$	$\log_{10} (T_1/T_2)$	Separation %
-192	.552	5.02	-192	.550	6.62	-192	.550	6.15
-174	.465	4.47	-176	.472	5.87	-174	.463	5.89
-157	.396	4.04	-143	.348	4.74	-159	.402	5.42
-150	.371	3.84	-134	.319	4.48	-144	.349	4.79
-135	.321	3.22	-124	.289	4.17	-137	.325	4.67
-125	.291	3.05	-114	.260	3.77	-130	.304	4.38
-99	.221	2.48	-94	.208	3.06	-121	.277	4.14
-86	.190	2.23	-84	.184	2.85	-107	.240	3.77
-80	.175	2.04	-75	.165	2.61	-82	.178	2.96
-70	.154	1.79	-70	.154	2.41	-29	.072	1.15
-31	.077	0.95	-49	.112	1.82			
			-33	.082	1.30			

Table 8. Hydrogen and carbon monoxide

$24.0\% \text{ H}_2$ $T_1 = 11.0^\circ \text{C.}$			$32.5\% \text{ H}_2$ $T_1 = 12.5^\circ \text{C.}$			$53.0\% \text{ H}_2$ $T_1 = 13.5^\circ \text{C.}$		
$T_2^\circ \text{C.}$	$\log_{10}$ $(T_1/T_2)$	Separation %	$T_2^\circ \text{C.}$	$\log_{10}$ $(T_1/T_2)$	Separation %	$T_2^\circ \text{C.}$	$\log_{10}$ $(T_1/T_2)$	Separation %
-192	.545	4.73	-192	.547	6.12	-192	.550	7.32
-142	.334	3.14	-170	.443	5.19	-167	.476	6.33
-124	.276	2.71	-158	.394	4.80	-145	.351	5.22
-102	.217	2.29	-140	.331	4.13	-130	.303	4.55
-90	.188	1.92	-126	.289	3.78	-107	.238	3.60
-76	.157	1.62	-117	.263	3.54	-89	.193	3.34
-63	.131	1.38	-103	.226	3.08	-93	.201	3.46
-40	.084	0.92	-88	.189	2.60	-63	.134	2.29
			-65	.138	1.94			

Table 9. Hydrogen and argon

Table 10. Hydrogen and oxygen

$47.0\% \text{ H}_2$ $T_1 = 13.5^\circ \text{C.}$			$55.6\% \text{ H}_2$ $T_1 = 16.5^\circ \text{C.}$			$29.8\% \text{ H}_2$ $T_1 = 17^\circ \text{C.}$		
$T_2^\circ \text{C.}$	$\log_{10}$ $(T_1/T_2)$	Separation %	$T_2^\circ \text{C.}$	$\log_{10}$ $(T_1/T_2)$	Separation %	$T_2^\circ \text{C.}$	$\log_{10}$ $(T_1/T_2)$	Separation %
-165	.425	5.19	-170	.448	5.78	-171	.452	4.07
-147	.358	4.40	-161	.412	5.43	-158	.400	3.74
-143	.344	4.24	-147	.361	4.96	-139	.334	3.43
-136	.321	4.09	-143	.348	4.81	-126	.295	3.15
-131	.304	3.91	-130	.307	4.18	-120	.277	2.96
-124	.283	3.67	-112	.258	3.72	-106	.239	2.62
-108	.238	3.42	-95	.212	3.30	-95	.212	2.35
-101	.220	3.11	-80	.176	2.80	-86	.190	2.09
-83	.177	2.74	-68	.152	2.54	-74	.163	1.81
-76	.162	2.43	-57	.128	2.01	-60	.133	1.45
-55	.118	1.79	-42	.098	1.57	-50	.112	1.26
-42	.091	1.40				-31	.078	0.88

Table 11. Nitrogen and argon

$46.0\% \text{ N}_2$ $T_1 = 16^\circ \text{C.}$			$62.5\% \text{ N}_2$ $T_1 = 16.5^\circ \text{C.}$			$70.0\% \text{ N}_2$ $T_1 = 17.5^\circ \text{C.}$		
$T_2^\circ \text{C.}$	$\log_{10}$ $(T_1/T_2)$	Separation %	$T_2^\circ \text{C.}$	$\log_{10}$ $(T_1/T_2)$	Separation %	$T_2^\circ \text{C.}$	$\log_{10}$ $(T_1/T_2)$	Separation %
-179	.486	1.14	-179	.488	0.95	-159	.407	0.92
-145	.354	0.92	-134	.319	0.87	-125	.294	0.77
-119	.274	0.83	-92	.212	0.73	-107	.244	0.72
-96	.213	0.77	-72	.159	0.59	-104	.232	0.72
-78	.171	0.65	-52	.118	0.46	-89	.199	0.67
-58	.129	0.55				-82	.181	0.59
-51	.115	0.50				-70	.156	0.54
-41	.095	0.40				-56	.123	0.42
						-44	.102	0.39

## EXPERIMENTS ON MAGNETOSTRICTIVE OSCILLATORS AT RADIO FREQUENCIES

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**ABSTRACT.** An account is given of the behaviour of two magnetostrictive oscillators 6 mm. and 4.5 mm. in length, when placed in a coil in series with the main induction coil of a simple valve-maintained oscillating circuit. The frequency characteristic of the smaller oscillator is 540 kc./sec.

### § 1. RÉSUMÉ OF PREVIOUS WORK

IN previous papers\* various experiments on the maintenance of mechanical oscillations by magnetostriction have been described. These experiments extended from frequencies of 2.5 to 270 kc./sec. in the case of longitudinal oscillations of nickel rods vibrating in their lowest modes with one node at the centre. The method employed at the higher frequencies was to surround the centre of the bar with a coil wound on a glass tube in which the bar could slide easily. This coil was in series with the main induction coil of a simple valve-maintained circuit of the tuned anode type. In the lead from the grid coil to the grid a microammeter was inserted to indicate the rectified grid current; this instrument served to show the effect of the reactions of the oscillations of the bar on the valve assemblage and also enabled frequencies to be determined by means of an absorption wave-meter. The bar was magnetised before insertion in the tube; the coil surrounding it carried the plate current in a direction to assist the permanent magnetism of the bar. In the previous experiments the polarisation due to these two causes was increased by placing the tube in the hollow axis of the two bored pole pieces of an electromagnet. With bars of nickel less than 1 cm. in length the current through the electromagnet could be dispensed with, the residual magnetism being sufficient; the pole pieces and electromagnet were replaced at still higher frequencies by a small permanent magnet placed near the oscillator.

By these means the experiments with nickel rods were carried down to a length of 8 mm. and a frequency of about 300 kc./sec. Pierce† having found "nichrome" to be a good material for use in magnetostriction experiments, the next shortest bar to be tried was made of "glowray," a material having the approximate composition 65 per cent. nickel, 20 per cent. iron, 15 per cent. chromium. A turned bar of glowray 7 mm. long and 2.13 mm. in diameter was annealed at a dull red heat in lime and after remagnetisation was found on testing to give a frequency of 356 kc./sec. This oscillator was shown in operation at the Exhibition of the Physical

\* *Nature*, Dec. 13, 1927; *Electrician*, Dec. 28, 1928; Jan. 4, 1929.

† *Proc. Am. Ac. of Arts and Science*, 63, 1-47 (1928).

and Optical Societies 1929 and an account of the experiment is included in Dr Ferguson's description of the Exhibits in the Research and Experimental Section in the *Journal of Scientific Instruments* for February 1929.

## § 2. APPARATUS

An account will now be given of similar experiments with two glowray bars, one 6 mm. long, the other 4.5 mm. long.

The experiments on these two bars were carried out under very similar conditions. The apparatus is shown diagrammatically in Fig. 1.  $L_1$  is the main induction coil. It consists of 20 turns of No. 20 D.W.S. copper wire wound close together in

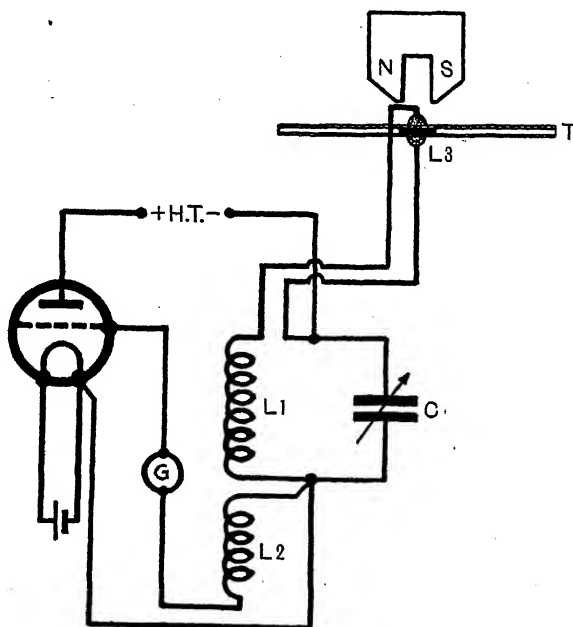


Fig. 1.

a single layer on a former of 9.5 cm. diameter. The grid coil  $L_2$  was a similar coil of 100 turns of No. 26 D.W.S. on a cylinder 8 cm. in diameter. It was mounted so as to be adjustable with respect to  $L_1$  by means of a simple geometric slide provided with a linear scale. The microammeter  $G$  of the moving coil type had a resistance of 10 ohms and was used unshunted. Its maximum deflection was obtained with  $240 \mu\text{A}$ . The coil  $L_3$  in series with  $L_1$  carries the plate current and the oscillatory current: It has 200 turns of No. 36 enamelled copper wire, wound on a thin-walled glass tube,  $T$ , Fig. 1. The glass tube was fixed in a V groove in an ebonite block, the magnet  $NS$  being placed on the bench near it. The oscillator was in a symmetrical position with respect to the windings of  $L_3$  and the poles of the permanent magnet.

The valve was a B.T.H. G P 210 and was operated at 1.9 volts on the filament and 50 volts on the plate, with no grid bias.

### § 3. EXPERIMENTS WITH GLOWRAY OSCILLATOR 6 MM. IN LENGTH

The oscillator was 2.135 mm. in diameter. It was not found possible to detect any magnetostrictive reactions on the galvanometer until after the bar had been annealed by heating to a dull red heat in lime. The effect of the oscillations of the bar in the coil  $L_3$  after magnetisation was then easily detected. The coupling between  $L_1$  and  $L_2$  was adjusted until these effects were well marked. The distance between the centres of the coils  $L_1$  and  $L_2$  was then about 3.5 cm. and the magnet faces  $N$  and  $S$  were about half a centimetre distant from the oscillator. Figs. 2 to 5 deal with the behaviour of this oscillator. The vertical axis on the left is graduated to indicate in the upper parts of the figures the rectified grid current in microamperes, in the lower parts the capacity of the wave-meter condenser in  $\mu\mu\text{F}$ , while the numbers on the horizontal axis show the value in  $\mu\mu\text{F}$  of the total capacity ( $C$ , Fig. 1) in the oscillatory circuit.

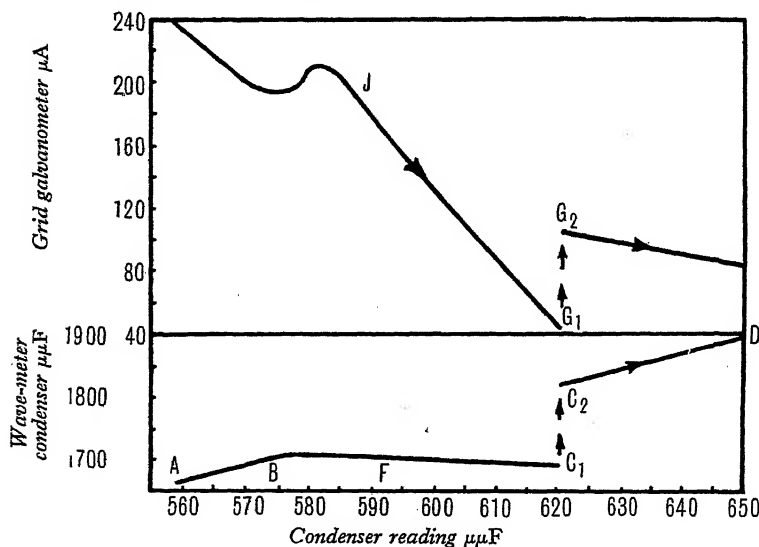


Fig. 2.

*Description of Fig. 2.* Starting with a small capacity  $C$  and a large grid current, the grid current falls steadily as  $C$  is increased until it reaches a minimum; the frequency which began to fall with rising capacity then becomes approximately stabilised. This is shown by the curve in the lower section of Fig. 2, the ordinates of which are the readings of the wave-meter condenser which were taken by closing the wave-meter circuit and adjusting for resonance immediately after recording the deflections of the grid galvanometer. While the value of  $C$  rises from 575 to 620  $\mu\mu\text{F}$  the settings of the wave-meter condenser are almost constant, a very small change being shown over this range. If the oscillator had not been free to vibrate, the wave-meter curve would have followed a practically straight track  $ABC_2D$ , the path  $BC_1C_2$  being replaced by the direct path  $BC_2$ .

The wave-length corresponding to  $1700 \mu\mu\text{F}$  on the figure is  $719 \text{ m.}$  and the frequency  $417 \text{ kc./sec.}$

As the capacity  $C$  is slowly increased from  $575 \mu\mu\text{F}$  the grid current reaches a maximum and then steadily decreases. When the capacity in the valve set reached  $620.5 \mu\mu\text{F}$  in the particular series of readings from which Fig. 2 was drawn the galvanometer deflection suddenly rose from  $G_1$  to  $G_2$ . The value of the condenser at which this discontinuity occurred varied over a few  $\mu\mu\text{F}$  in different experiments. When the grid current rises from  $G_1$  to  $G_2$  the frequency drops from that corresponding to  $C_1$  to that corresponding to  $C_2$ . The oscillator, although still probably executing forced vibrations, exerts little effect on the frequency of the electrical oscillations, so that the path of the wave-meter condenser readings from  $C_2$  to  $D$  is sensibly the same as if the oscillator were clamped.

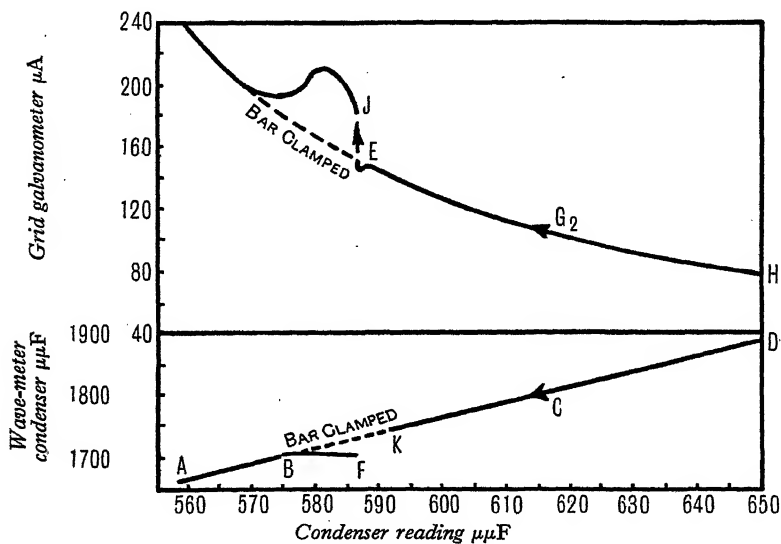


Fig. 3.

The increase in the capacity of the oscillating condenser  $C$  from  $580$  to the capacity at which the grid current suddenly rises is accompanied by a decrease in the wave-length and an increase in the frequency of the oscillations.

*Description of Fig. 3.* The values of the grid current and wave-length are not repeated as the condenser readings are traversed in the opposite direction.

Starting with a large condenser reading and a small grid current, Fig. 3 indicates the changes in grid current and wave-meter condenser as the capacity in the maintained circuit is decreased. The grid current steadily rises and the frequency increases as the capacity in the maintained set is diminished until at about  $587 \mu\mu\text{F}$  the grid current drops slightly at  $E$ ; on further decreasing the capacity the grid current rises slightly, but any further decrease in  $C$  now causes the galvanometer trace to increase suddenly to  $J$ , and the wave-meter condenser trace drops to the point  $F$ . The oscillating bar is now controlling the frequency. On further traversing

the curves to the left the paths are sensibly the same as the corresponding portions of the curves shown in Fig. 2. If when the grid galvanometer curve had reached  $E$ , Fig. 3, the capacity had been again increased, the upper and lower curves would have been retraced in the direction  $EG_2H$  and  $KCD$ .

*Description of Fig. 4.* If the sudden discontinuity has occurred and the grid current has jumped to  $J$  and the wave-meter condenser curve to  $F$ , then these curves cannot be traced from left to right; that is, this discontinuity only occurs in the sense from  $E$  to  $J$  and  $K$  to  $F$ . This is illustrated in Fig. 4.

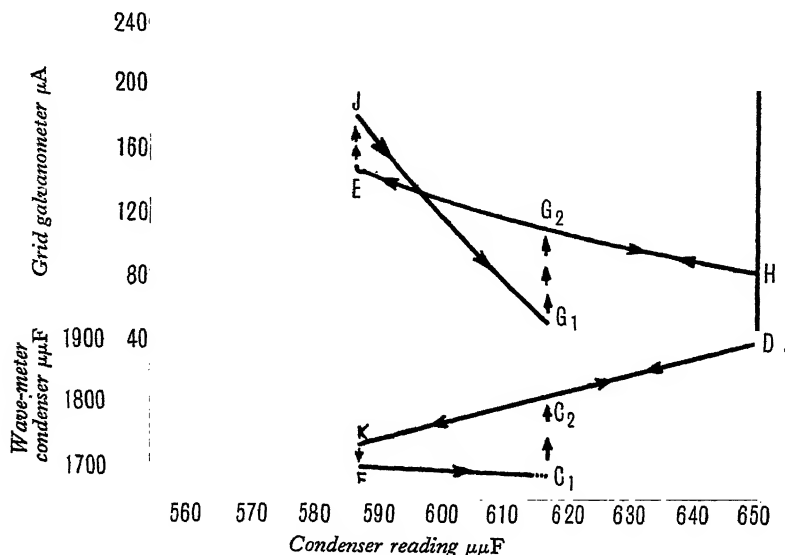


Fig. 4.

In this figure the capacity was initially  $650 \mu\mu F$ , and is decreased until the bar takes control of the frequency when the grid galvanometer has jumped from  $E$  to  $J$ . The capacity is then increased; the curves  $J$  to  $G_1$  and  $F$  to  $C_1$  are traced when the discontinuity occurs in both; the bar now loses control and the galvanometer and wave-meter condenser readings rise from  $G_1$  to  $G_2$  and from  $C_1$  to  $C_2$ . If  $C$  is still further increased, the return tracks traverse the original paths which commenced the experiment.

If, having started as in Fig. 2, we increase the capacity to a value just insufficient to cause the discontinuity in the neighbourhood of  $620 \mu\mu F$ , we may retrace the curves in the sense  $FBA$  and  $G_1J$  without encountering any discontinuity.

Returning to Fig. 4, it will be seen that there are for each value of  $C$  between certain limits two possible frequencies and two possible grid galvanometer readings. The lines  $FC_1$ ,  $JG_1$  correspond to the stabilised state and  $KC_2$ ,  $EG_2$  to the un-stabilised state.

If the filament battery is left on the valve permanently but the plate battery switched on for different values of  $C$ , the following results are obtained. For all values of  $C$  greater than that corresponding to the points  $J$ ,  $E$ ,  $K$ ,  $F$  the galvanometer

rose to the value indicated by the line  $EG_2H$ , indicating that the assemblage was oscillating in the unstabilised state. For all settings of  $C$  less than that given by  $J, E, K, F$  the galvanometer rose to points given on the curve to the left of  $J$  in Fig. 3.

For values of  $C$  corresponding closely to that given by  $J, E, K, F$  the galvanometer at first indicates an unstabilised vibration and then its pointer moves very soon afterwards to the upper stabilised position.

An example of oscillation hysteresis somewhat similar to that described above is given by Pierce\* who employed a different circuit.

#### § 4. EXPERIMENTS WITH DAMPED BAR

After the above experiments had been performed, powdered paraffin wax was packed into the glass tube to fill up those parts not occupied by the bar. The wax was melted by a hot wire, and after it had been cooled the results shown in Fig. 5

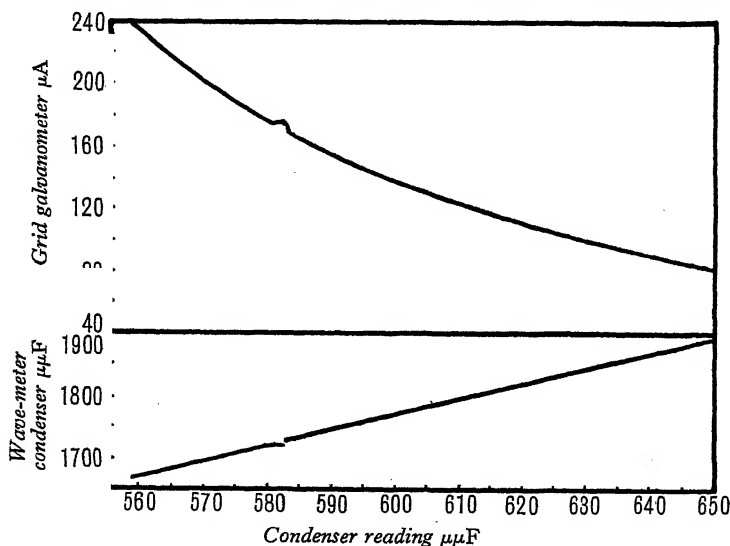


Fig. 5.

were obtained. The bar still showed signs of oscillating. The galvanometer and wave-meter curves were the same, no matter in which direction they were traced. The frequency indicated as stabilised when the capacity was near  $582 \mu\mu F$  is lower than the frequency when the bar is free. The attachment of the wax thus increases the inertia more than the restoring forces of the bar. This experiment was reproducible provided the temperature of the laboratory was low. A comparatively slight rise of temperature (three or four degrees Fahrenheit) sufficed to obliterate the effects altogether. The two curves of Fig. 5 then became quite regular, showing that when the wax was softened its viscosity prevented the bar from oscillating appreciably. The resulting curves have been drawn in as broken lines on Fig. 3, and the parts which do not lie on the previously drawn curves marked "bar clamped."

\* *Loc. cit.*



# § 5. EXPERIMENTS WITH GLOWRAY OSCILLATOR 4.5 MM. IN LENGTH

This oscillator was 2.178 mm. in diameter. After being annealed and magnetised it was placed in the same tube and surrounded by the same coil that was used for the experiments with the 6 mm. bar. There was no difficulty in finding evidence of the reaction of the bar on the oscillating set when the capacity was decreased. The grid current after decreasing rose suddenly when the capacity was so large that the bar could no longer control the frequency. On reversal of the capacity changes no evidence of reaction was at first evident, but by altering the distance of the polarising magnet and adjusting the position of the grid coil the sudden change in the conditions governing the oscillations was shown also in this direction.

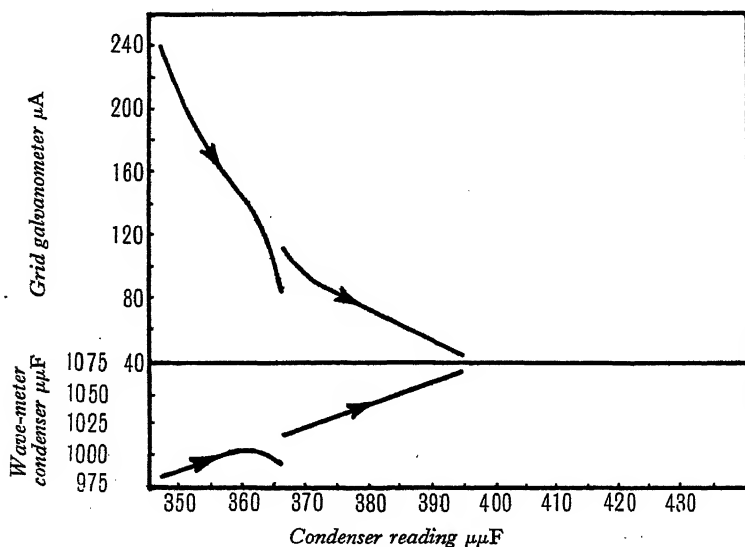


Fig. 6.

The distance between the centres of the coils  $L_1$  and  $L_2$  was then about 13.75 cm. and the magnet faces  $N$  and  $S$  were about 3 cm. distant from the oscillator. It will be noticed that both the permanent polarising field due to the magnet and the mutual inductance between the grid and anode coils are much less than in the case of the preceding experiments with the longer bar. Otherwise the conditions of the experiments were as nearly as possible identical.

*Description of Fig. 6.* The curves on this figure are traced from left to right. The discontinuity in the neighbourhood of  $C = 366 \mu\mu\text{F}$  is well marked. The frequency corresponding to  $1003 \mu\mu\text{F}$  on the wave-meter condenser is 540 kc./sec. corresponding to 556 m.

*Description of Fig. 7.* When the grid galvanometer and wave-meter condenser curves are drawn with decreasing capacity, the discontinuity occurs at a smaller

value of  $C$ . In this case, in contrast to that shown in Fig. 3, there is a sudden drop in the grid current at the stage when the bar assumes control of the frequency.

Probably much higher frequencies could be obtained from thinner and shorter bars by modifying the apparatus. Experiments on the subject are in progress.

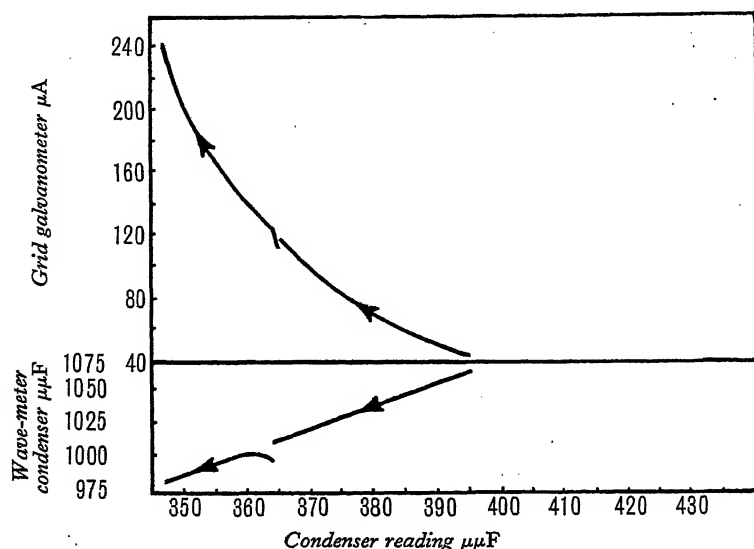


Fig. 7.

## DISCUSSION

Prof. R. W. WOOD, who was welcomed by the President on behalf of the Society, enquired whether the author had produced oscillations in single crystals, in order to see whether their crystal structure could be affected?

Dr C. V. DRYSDALE: The magnetostrictive effects mentioned by Dr Vincent are of great interest, but I should like to ask whether the bar was laminated, as at these high frequencies eddy currents must have a very serious influence and it seems probable that a highly laminated specimen would show the effects on a much larger scale than a solid one. The application of magnetostriction to acoustics seems likely to be very valuable, and Dr Vincent is to be congratulated on having shown its possibilities for radio frequencies.

Prof. C. L. FORTESCUE: The great interest of the paper lies in the fact that the actual range of variation over which the control can be exercised is given numerically, and in Fig. 2. Here, with a range of  $C$  from 575–620, the arrangement gives practically constant frequency. In other ways, the system behaves exactly like any coupled circuit maintained in oscillation by a self-excited valve.

It would be interesting to know whether the eddy currents take any part in maintaining the oscillations. The penetration under the conditions described is such that

90 per cent. of the changes are confined to less than half a millimetre in thickness. It seems likely that the forces arising from the eddy currents may be about 5 dynes, or thereabouts. If Dr Vincent has any information with regard to the damping, it would be possible to settle whether the phenomena are due to eddies or magnetostriction.

Prof. HOPWOOD: I should like to add my congratulations and to mention that I have succeeded in producing high-frequency oscillations by (apparently) making use of the Johnsen-Rahbek effect.

Dr OWEN: I should like to express my interest in the work of Dr Vincent on the stabilisation of an oscillating valve circuit by use of the phenomenon of magnetostriction. In regard to the question of obtaining constant standards of frequency in radio work, it is natural to compare this method, with its magnetic reaction on the tuned circuit, to the piezo-electric method, with its electric reaction. Has the author any data as to the temperature-coefficient of frequency of his glow-ray rods? His success in obtaining frequencies as high as half a million per second is presumably largely due to the high specific resistance of this material and the consequent reduction of damping due to eddy currents.

One would like to know the interpretation of the particular form of the curves found by the author. It would seem preferable to include the coil  $L_3$  on the condenser side of the tuned circuit  $CL_1$ , rather than on the inductance side, since in the latter case the variation with  $C$  of the plate current constitutes an unnecessary variation of the polarisation of the bar. The rise of frequency of the system as the capacity  $C$  is increased seems somewhat paradoxical; perhaps it is due to the oscillatory current growing stronger as  $C$  increases over the range  $BC_1$  (Fig. 2), since the effect of increasing the energy of the maintaining system is in general to raise the frequency of the maintained vibration.

Dr ECCLES: I should like to ask Dr Vincent if he has tried to find experimentally a tuned electrical circuit which can be coupled to the valve circuit so as to give discontinuous curves approximately similar to those given by the magnetostrictive oscillator. Such an attempt would bring out the differences between these mechanical systems and the most realisable equivalent electrical system. I must also express the appreciation felt by the audience with regard to Dr Vincent's beautiful and novel experiments.

AUTHOR'S reply: Although measurements of static magnetostriction have been carried out on single crystals of iron\*, and of nickel†, I do not know of any work having been done on dynamic magnetostriction with single crystals. My work has been done only with poly-crystalline materials. Prof. Wood's suggestion would form a most promising basis for research by someone familiar with the technique of single crystal growth and X-ray crystallography.

Solid magnetostrictive oscillators must presumably function less efficiently than

\* Webster, *Proc. Roy. Soc. A*, 109, 570-584 (1925); Honda and Mashiyama, *Tohoku University Sci. Rep.* 15, 755-776 (1926).

† Mashiyama, *Tohoku University Sci. Rep.* 17, 944-961 (1928).

highly laminated bars having similar elastic properties. The difficulty in applying Dr Drysdale's idea lies in the preservation of the elastic properties of the composite structure. Ordinary transformers hum a note which is due to the forced magnetostrictive vibrations of the laminated structure arising from the varying magnetic field. I hope to find the opportunity of working on the resonant vibrations of laminated oscillators at low frequencies. A split tube of nickel is a convenient low-frequency oscillator, but if one is aiming at a high intensity of sound the gain due to elimination of eddy current losses is largely offset by the decrease in the inertia and restoring forces as compared with those arising in the case of a solid bar.

With regard to the range over which the oscillator controls the frequency of the set, a point commented on by Prof. Fortescue, it should be stated that this varies very much with the constants of the apparatus. I have been in the habit of picturing the oscillating bar and its coil as constituting a system approximating to Butterworth's Class A\*. If this is legitimate, then the bar and its coil could be replaced by a coil in series with a parallel combination of  $L$ ,  $C$  and  $R$ . The eddy current loss could be allowed for by another inductance with mutual inductance to the coil of the bar in series with a resistance. The  $L$  of the equivalent circuit must be pure and thus it seems impossible to reproduce the effects of the oscillating bar by the substitution of a real circuit which is to be its equivalent at all frequencies. Electromagnetic deforming forces must be in operation when the bar is solid or when an unsplit tube is used as an oscillator. I am inclined to think that such forces, though perhaps not negligible, are very small compared with those due to magnetostriction. The reasons for this are that the oscillators which show the most striking effects are those such as nickel and its alloys, and iron and its alloys, which are known to have high coefficients of the direct static magnetostrictive or Joule effect. I have succeeded in getting distinctly audible sound from a bar of commercial aluminium which I attributed to magnetostriction†, but I am now not certain that the results should not be regarded as due to the forces of electromagnetic origin contemplated by Prof. Fortescue. I have not succeeded in getting any such effects with brass. I hope to return to experiments on these matters, which are profoundly obscure though exceedingly interesting.

The evaluation of damping to which Prof. Fortescue refers might probably be effected by methods similar to those used by Dye in his researches on crystal resonators‡.

I am interested to hear of Prof. Hopwood's experiment and hope that he will give a fuller account of the work to the Society. It seems that Prof. Hopwood has added a new method of electrically maintaining a high-frequency mechanical vibration to those already known.

Prof. Pierce§ has published data which answer Dr Owen's first enquiry. I understand that "glow-ray" and "nichrome" are practically synonyms. Nickel is, I think, just as suitable as glowray except that, according to Pierce, it has a higher temperature coefficient of frequency.

\* *Proc. Phys. Soc.* 27, 410-424 (1915).

† *Ibid.* 38, 399-458 (1926).

‡ *Electrician*, loc. cit.

§ *Loc. cit.*

Dr Owen suggests putting the bar and coil in the condenser branch of the oscillatory circuit. In the interval between the preparation of the paper for the press and its reading before the Society, I had carried out a series of experiments on the 6 mm. glow-ray bar intended to throw light on the comparative behaviour of an oscillatory circuit when the bar and coil were switched into either of its branches. The pivot of the two-way switch was joined to the negative terminal of the high-tension battery and the ends of the coil  $L_3$  (Fig. 1) were connected to the other two electrodes of the switch. One of these was joined to  $L_1$  and the other to  $C$  so that on moving the switch arm  $L_3$  could be thrown into either branch of the anode fly-wheel. The coil  $L_1$  was changed for a similar one of 30 turns of No. 24 D.W.S. copper wire. The other conditions were as given in the paper. The grid coil and main inductance coil had to be more closely coupled when  $L_3$  was put in the capacitive branch than when in the inductive branch. The centres of the coils were 4.2 cm. and 5.9 cm. apart in the two cases. The comparison is thus not strictly between the two positions of  $L_3$  but includes effects due to the altered position of the grid coil. The results as regards control can be seen from the following table:

		Capacity $\mu\mu F$		Range
Capacity decreasing }	$L_3$ in capacitive branch	487	507	20
	„ inductive „	448	458	10
Capacity increasing }	$L_3$ in capacitive branch	487	528	41
	„ inductive „	448	484	36

In this particular series of experiments the control is greater when the bar and coil are in the condenser branch. The peaks of the grid current curves are also more pronounced. In addition to the advantage of constant polarisation the arrangement has the convenience that the sense of winding of  $L_3$  is immaterial.

In reply to the President: I have not done any experiments on the imitation of the effects of the oscillator by means of a coupled circuit. Although such a circuit could not, I think, quite adequately replace the bar, the suggested experiments would be very interesting. One reason why I have not tried such substitution experiments is that I know of no ready means of efficiently clamping and unclamping an oscillator. This applies to large bars and small ones. Any clamping method I have tried is somewhat tedious in that on unclamping it is difficult to reproduce the exact conditions which existed before clamping.

I wish to thank the President and those Fellows who took part in the discussion for the interest they showed in the paper and for their very kind congratulations.

# THE ABSOLUTE MEASUREMENT OF SOUND INTENSITY

By F. D. SMITH, M.Sc., Admiralty Research Laboratory, Teddington

*Communicated by Dr A. B. Wood April 9, 1929.*

*Read and discussed June 28, 1929*

**ABSTRACT.** An absolute measurement of sound pressure is described in which the sound is received with a moving-coil receiver. The signal heard after suitable amplification is compared with the signal produced by a small known electromotive force  $v$  applied to the receiver. It is shown that when the two signals are equal in intensity the following simple relation connects the total sound pressure  $P$  on the receiver with the electromotive force  $v$ ,

$$P = vHl/z_m,$$

where  $H$  is the strength of the magnetic field in which the moving coil, consisting of a length  $l$  of wire, moves, and  $z_m$  is the motional impedance of the receiver at the frequency of the sound. It is shown that the phase also of the sound can be determined with the aid of a phase-shifting transformer. Since the measurement is independent of the amplifying circuit, it is possible to use a high degree of amplification and very feeble sounds may therefore be measured.

## § 1. INTRODUCTION

**M**ETHODS of measuring sound intensity may be roughly classified into two groups, those in which a directly measurable effect is produced by the sound and those in which the unknown sound pressure is compared with a known force, produced electrically. The classical methods are included in the first group, for example, the Rayleigh disc where the sound produces a measurable torque on a suspended disc\*, and the torsion pendulum where the radiation pressure of sound on a reflecting obstacle in its path is measured. Langevin† and Boyle‡ have used the torsion pendulum for the measurement of intense high frequency sounds in water. Tucker and Paris§ have made absolute measurements of sound intensity by measuring the change of resistance of a thin hot wire in a sound field. Unfortunately, a very intense sound is needed to produce directly measurable effects, and resonators must often be used to reinforce the sound. Even with the help of resonators, the direct methods are limited to fairly loud sounds. For the measurement of feeble sounds, one of the methods of the second group must be

\* Lord Rayleigh, *Theory of Sound*, 2, 44-45 (1896).

† Langevin, *International Hydrographic Bureau, Monaco: Special Papers*, No. 3, 1924; No. 4, 1926.

‡ R. W. Boyle, *Proc. Roy. Soc. Canada*, III, 167 (1925).

§ Tucker and Paris, *Roy. Soc. Trans.* 221, 389 (1921).

used. The compensation method proposed by Gerlach\* is a typical example. A metal strip exposed on one side to the sound waves lies between the poles of a magnet. The pressure of the sound on the strip sets it into vibration and an alternating current is passed through the strip of such magnitude, frequency and phase that it brings the strip to rest. The sound pressure on the strip is then equal to the electromagnetic force on it, which can be calculated from the known current and magnetic field. Very sensitive arrangements for detecting the motion of the strip have been devised. A similar compensation method in which the sound pressure is balanced against the electrostatic force between the plates of a condenser microphone is described by Meyer†.

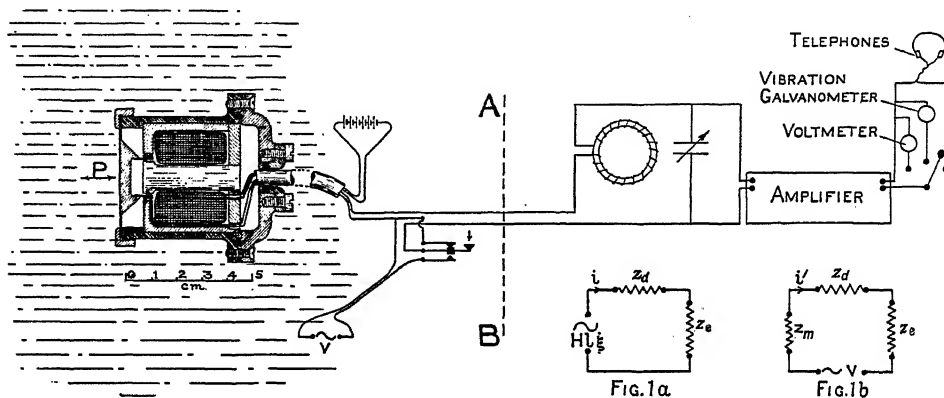


Fig. 1. Circuit diagram for measurement of sound pressure.

The method described here resembles those of Gerlach and Meyer in that it depends upon a balance between the effects produced on a sensitive amplifying circuit by the unknown sound wave and a known small electromotive force. A moving-coil receiver, shown in Fig. 1, is connected to a sensitive receiving circuit consisting of a tuned circuit and a multistage valve amplifier. A sound wave falling upon the receiver produces a deflection of a voltmeter, or a vibration galvanometer, or a note in telephones connected to the output of the valve amplifier, the choice of indicating instrument depending on the frequency of the sound to be measured. Arrangements are made for applying to the receiver a small known electromotive force of the same frequency as the sound wave. The sound wave and the electromotive force act alternately, and the magnitude of the latter is adjusted until both produce the same deflection of the indicating instrument. It can be shown that when this condition is fulfilled a simple formula gives the magnitude of the sound pressure on the receiver in terms of the known electromotive force and three easily measured constants of the receiver. These constants are the length of wire in the moving coil, the strength of the magnetic field in which it moves and its motional impedance at the frequency of the sound wave. To find the formula it is necessary to calculate separately the effects of the sound pressure and the electromotive force.

\* Gerlach, *Wiss. Veröff. aus d. Siemens-Konzern*, 3, 139 (1923); *Handbuch der Physik* 8, *Akustik*, pp. 572-580 (Springer, 1927).

† E. Meyer, *Zeits. Tech. Physik*, 7, 609-616 (1926).

§ 2. EQUATIONS OF MOTION

The receiver shown in Fig. 1 is suitable for the reception of sound in water, but it can represent any moving-coil receiver receiving sound in any medium. It consists of a rigid circular piston of effective area  $A$  supported on an elastic edging which resists a displacement  $\xi$  with a force  $G\xi$ . A coil of a length  $l$  of wire rigidly attached to the piston lies in a magnetic field of strength  $H$ . The effect of the medium in contact with the piston can be represented by an addition to its mass of  $M_w$  and a damping force  $N_w\dot{\xi}$ . When the piston moves with simple harmonic motion with instantaneous velocity  $\dot{\xi}$  the medium opposes the motion with a force

$$M_w\ddot{\xi} + N_w\dot{\xi}.$$

Let  $P$  represent the total force on the piston due to a sound wave falling on it when it is prevented from vibrating, where

$$P = P_0 e^{j\omega t}.$$

This force becomes

$$P - M_w\ddot{\xi} - N_w\dot{\xi},$$

when the piston is released and begins to vibrate with velocity  $\dot{\xi}$ . It has to overcome the inertia  $M$  of the piston and the coil, the stiffness  $G$  of the coil support, the internal mechanical friction  $N_i$  and the electromagnetic force on the coil. The equation of motion is therefore

$$P - M_w\ddot{\xi} - N_w\dot{\xi} = M\ddot{\xi} + N_i\dot{\xi} + G\xi + Hli,$$

where  $i$  represents the instantaneous current flowing in the coil. When the equation is re-written

$$P = (M + M_w)\ddot{\xi} + (N_w + N_i)\dot{\xi} + G\xi + Hli,$$

it becomes clear that it can be expressed in the form

$$P = Z\dot{\xi} + Hli \quad \dots\dots(1),$$

because  $\ddot{\xi} = j\omega\dot{\xi}$  and  $\xi = \dot{\xi}/j\omega$  for simple harmonic motions.  $Z$  represents the total mechanical impedance of the receiver. An equation can be obtained relating the current  $i$  flowing in the coil to the velocity of the coil. The current  $i$  depends upon the impedance of the external circuit to which the coil is connected. The whole of the receiving circuit to the right of the line  $AB$  in Fig. 1 can be represented by a complex impedance  $z_e$ , and the whole circuit takes the simple form shown in Fig. 1 (a), in which  $z_d$  represents the damped impedance of the coil, that is, its impedance when motion is prevented, and  $Hl\dot{\xi}$  is the electromotive force induced by the motion of the coil in the magnetic field. We may write

$$Hl\dot{\xi} = (z_d + z_e)i \quad \dots\dots(2),$$

and  $\dot{\xi}$  may be eliminated from (1) with the following result,

$$P = \{Z(z_d + z_e)/Hl + Hl\}i \quad \dots\dots(3).$$

This equation gives the current  $i$  flowing to the external circuit when a force  $P$ , due to the sound, acts on the receiver.

When the electromotive force  $v$  acts upon the circuit instead of the sound pressure, a current  $i'$  flows in the external circuit depending upon the total electrical im-



pedance. The whole circuit is equivalent to that of Fig. 1 (b) in which the motional impedance  $z_m$  of the moving coil must be included because the current  $i'$  sets the coil into vibration. We may write

$$v = (z_d + z_m + z_e) i' \quad \dots\dots(4).$$

The indicating instrument at the output of the amplifier gives the same reading for the sound pressure  $P$  and the electromotive force  $v$  when  $i = i'$ , that is when

$$\frac{P}{Z(z_d + z_e)/Hl + Hl} = \frac{v}{z_d + z_m + z_e} \quad \dots\dots(5),$$

from equations (3) and (4).

This relation between  $P$  and  $v$  can be simplified by eliminating  $Z$  or  $z_m$  as follows. A current  $i'$  in the coil of the receiver results in a mechanical force  $Hli'$  which sets the coil into vibration with a velocity  $\dot{\xi}$  of magnitude  $Hli'/Z$ . This motion of the coil in the magnetic field induces in it an electromotive force of  $Hl\dot{\xi}$ , that is  $H^2l^2i'/Z$ , which must be equal to  $z_m i'$  by the definition of motional impedance. Therefore

$$z_m = H^2l^2/Z \quad \dots\dots(6).$$

### § 3. RELATION BETWEEN SOUND PRESSURE AND ELECTROMOTIVE FORCE

The result of eliminating  $Z$  from (5) by means of (6) is

$$P = vHl/z_m \quad \dots\dots(7),$$

and the result of eliminating  $z_m$  is

$$P = vZ/Hl \quad \dots\dots(8).$$

These are the two formulae upon which this method for the absolute measurement of sound pressure depends. The first involves  $z_m$ , the motional impedance of the moving coil, and the second involves  $Z$ , the total mechanical impedance of the receiver. If the receiver is resonant at the frequency of the sound, its motional impedance is easy to measure and (7) is used. If the receiver is resonant at a frequency much higher or lower than that of the sound, this motional impedance is too small to measure and it is necessary to determine the mechanical impedance  $Z$ . From the equation of motion (1),

$$Z = j\omega (M + M_w) + (N_w + N_i) + G/j\omega,$$

where  $j = (-1)^{\frac{1}{2}}$  and  $\omega = 2\pi \times \text{frequency}$ .  $Z$  is very nearly equal to  $j\omega (M + M_w)$  when the resonance frequency of the receiver is much lower than the frequency of the sound, and very nearly equal to  $G/j\omega$  when it is much higher. In the first case the effective mass of the vibrating parts of the receiver is required, and in the second case the stiffness of the support. Both of these quantities can be found with sufficient accuracy provided that the receiver is suitably designed.

The resonant receiver is a very sensitive arrangement, but it is limited to the narrow range of frequency in the neighbourhood of its resonant point where the motional impedance is appreciable. The non-resonant receiver can be used over a

wide range of frequency, but it is relatively insensitive, a disadvantage which can be partly overcome by the use of a receiving circuit giving a high overall amplification.

It is worthy of note that the impedance of the external circuit  $z_0$  and the damped impedance of the moving coil do not appear in equations (7) and (8), a somewhat unexpected result since the amplitude of vibration of the receiver does depend upon the impedance of the circuit connected to it. The measurement is independent of these impedances and any convenient amplifying circuit may be used. In particular, the resistances in the leads connecting the receiver to the amplifying circuit do not affect the measurement, and the amplifier may be placed at a convenient distance from the region in which the sound waves are travelling.

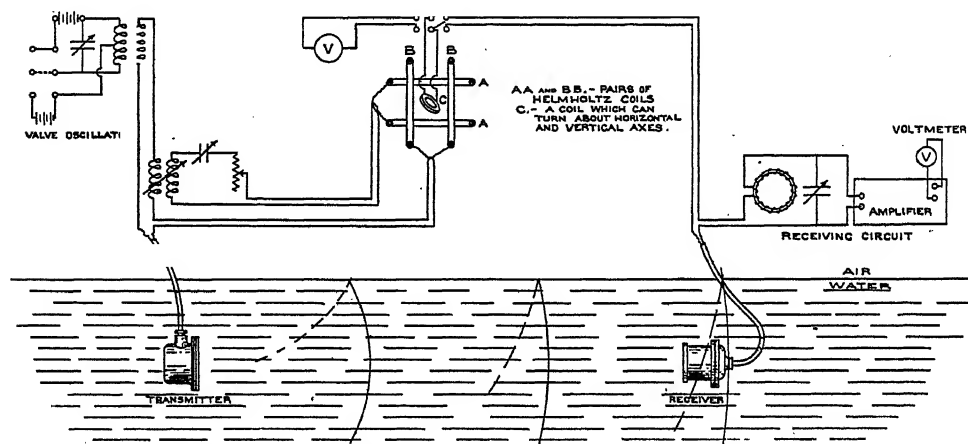


Fig. 2. Phase and amplitude measurement with a phase-shifting transformer.

The measurement gives the total sound pressure on the receiver when it is prevented from vibrating. In some special cases the sound pressure  $p$  per unit area in the medium when the receiver is removed can be inferred. If the dimensions of the receiver are small compared with the wave-length of the sound, the pressure  $p$  is given by

$$P = pA,$$

where  $A$  is the area of the vibrating face of the receiver. If a receiver of any size is supported by a large rigid plane plate on which the sound falls normally, the pressure is doubled by reflection and

$$P = 2pA.$$

Finally, a receiver with a plane receiving surface large compared with the wave-length on which the sound falls normally is subject to a total pressure  $P$ , where

$$P = 2pA.$$

These are the only three cases from which the sound pressure in the undisturbed medium can immediately be inferred from the sound pressure on the receiver. Receivers comparable in size with the wave-length are subject to a total pressure

$P$  which lies between the values  $pA$  and  $2pA$ . The calculation of the exact value involves the calculation of the diffraction and scattering of sound by the receiver considered as an obstacle in the path of the sound. The solution given by Rayleigh for a spherical obstacle has been applied by Ballantine\* to sound intensity measurements with a condenser microphone. He supported the microphone inside a spherical case so that its receiving surface formed part of the surface of the sphere, and, by calculating the diffraction and scattering of sound by the sphere, found the pressure on the microphone in terms of the pressure in the undisturbed medium. He was thus able to use a receiver comparable in size with the wave-length for the absolute measurement of sound intensity.

#### § 4. MEASUREMENT OF MAGNITUDE AND PHASE

The relations between  $P$  and  $v$  given in equations (7) and (8) hold when both produce the same current in magnitude and phase in the external circuit. If the phase of  $v$  is changed by half a period, the current produced by it changes in phase by the same amount and becomes opposite in phase to the current produced by  $P$ . The application of  $P$  and  $v$  simultaneously to the circuit then produces no current in the external circuit and a null measurement results. By varying  $v$  in magnitude and phase until there is no deflection at the output of the amplifier, a balance between  $P$  and  $v$  is obtained which is expressed by the relations

$$P = -vHI/z_m \quad \text{.....(9),}$$

and

$$P = -vZ/HI \quad \text{.....(10),}$$

from either of which the magnitude and phase of  $P$  can be calculated.

The alternating electromotive force variable in magnitude and phase can be obtained from an alternating current potentiometer. The instruments in which the magnitude and phase of the known electromotive force are separately variable are more convenient for sound measurements than those which resolve the electromotive force into two components at right angles†. The conversion of the rectangular components to polar components is inconvenient when many readings have to be made. For this reason the phase-shifting transformer shown in Fig. 3 has been designed to provide the variable electromotive force. It may safely be used at the highest sonic frequencies, as the use of metal in its construction is avoided. A pair of equal co-axial circular coils at a distance apart equal to their radius is fixed at right angles to another similar pair of coils. When one pair of coils carries an alternating current equal to but in quadrature with the current in the other pair of coils, a rotating magnetic field is produced inside the arrangement. A movable coil supported in this rotating field can be turned about horizontal and vertical axes. The rotation of the coil about a horizontal axis controls the magnitude of the

\* Stuart Ballantine, "Effect of diffraction around the microphone in sound measurements," *Phys. Rev.* **32**, 988, 992 (1928).

† A. Campbell, "A new alternating current potentiometer of Larsen type," *Proc. Phys. Soc.* **41**, 94-8 (1928). See the discussion. C. V. Drysdale, *Proc. Phys. Soc.* **21**, 561-571 (1909); *ibid. Electrician*, **75**, 157-160 (1915).

electromotive force induced in it, and its rotation about a vertical axis controls the phase. The disposition of each pair of fixed coils is that shown by Helmholtz to produce a fairly uniform field in the space in which the movable coil lies. The range of electromotive force obtained by rotating the movable coil about a horizontal axis is extended by providing coils with various numbers of turns. The sets of standard coils sold for broadcast reception are suitable for this purpose, as they have the

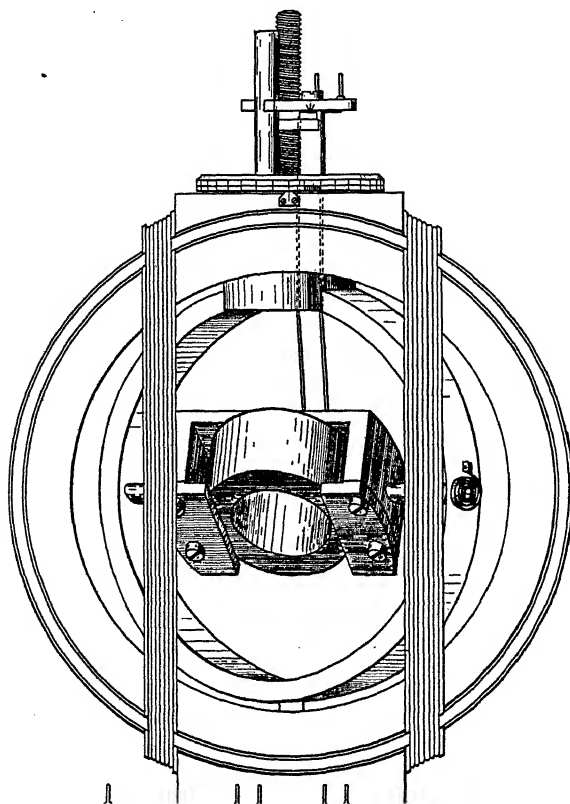


Fig. 3. Phase-shifting transformer.

same overall dimensions and are readily interchangeable in the phase-shifting transformer. In another convenient arrangement for changing the range of the instrument, the fixed coils are wound in two parts which can be connected in series or in parallel and, further, each pair of fixed coils may be in series or in parallel. These changes are sufficient to provide a very wide range of electromotive force.

The movable coil is carried on a vertical wooden ring which rotates about a vertical axis inside the fixed coils, its angular position being shown on a circular scale and pointer at the top of the instrument. The electrical connections to the movable coil are made by two flexible conductors running from the coil through the top of the instrument to a pair of terminals. These terminals are fixed in a block,

and by the raising and lowering of this block with a screw micrometer the coil can be turned about a horizontal axis. Two spiral springs, one of which is seen in Fig. 3, turn the coil against its electrical connections and keep the latter taut, thus preventing any back-lash. The micrometer reading is easily converted into the corresponding circular position of the coil. Wood and ebonite are used in the construction of the instrument, metal being avoided as much as possible because of its effect in distorting the magnetic field.

The external electrical connections to the instrument are shown in Fig. 2, where the instrument itself is drawn diagrammatically in plan. One pair of fixed coils carries the same current as the source of sound, while current for the other pair of coils is derived from a mutual inductance and a resonant circuit. When this circuit is adjusted to resonance, the currents in the two pairs of coils are in quadrature and can now be made equal by adjustment of the variable resistance in the resonant circuit. To test the adjustment of the two currents for equality and quadrature the movable coil is connected to a voltmeter and the deflections as the coil is rotated about a vertical axis are observed. The deflection of the voltmeter should be independent of the angular position of the moving coil. In the practical use of the instrument this condition is found by trial, and then calibration is carried out with the aid of the voltmeter and an ammeter in series with the fixed coils.

The magnitude and phase of the electromotive force which balances the sound pressure are known from the calibration and the geometry of the phase-shifting transformer. It remains to infer the magnitude and phase of  $P$  from equation (9) or (10). Writing

$$P = P_0 e^{j\omega t},$$

$$v = v_0 e^{j(\omega t + \alpha)},$$

and

$$z_m = |z_m| e^{j\beta},$$

where  $j = (-1)^{\frac{1}{2}}$ ,  $\omega = 2\pi \times$  frequency,  $|z_m|$  represents the magnitude of the motional impedance and  $\tan \beta$  is the ratio of motional reactance to motional resistance it appears from (9) that

$$P_0 = -\frac{v_0 H l}{|z_m|} \times e^{j(\alpha - \beta)} \quad \dots\dots(11),$$

which shows that

$$\alpha - \beta = \pi,$$

and

$$P_0 = v_0 H l / |z_m|.$$

Since the angle  $\beta$  is known from the motional impedance, the angle  $\alpha$  which is the phase difference between the sound pressure and the electromotive force is also known. For the special case of a receiver used at its resonance point, the motional impedance reduces to a pure resistance,  $\beta$  is zero and the sound pressure and the electromotive force have opposite phases. Similar formulae for the magnitude and phase of  $P$  can be derived from (10) if the receiver is to be used at a frequency remote from its resonance point.

It is often sufficient to measure sound pressure regardless of phase: a source of known small electromotive force of the same frequency as the sound to be measured

is required. Davis and Littler\* used a calibrated mutual inductance, through the primary of which they passed the alternating current to their source of sound. When the source of sound is mechanically driven or at an inconveniently large distance from the receiver, it is necessary to provide a separate valve oscillator generating the small electromotive forces. A suitable circuit has been described by the author with B. S. Smith†, and in the same place references to other methods of producing small known electromotive forces will be found. The phase of the sound being measured is in this case meaningless, and the null measurement in which the sound pressure is balanced against the electromotive force cannot be used. The sound pressure and the electromotive force must be applied alternately to the receiving circuit, and the electromotive force adjusted until both produce the same deflection of the indicating instrument.

Measurements of phase only are easily made with a microphone receiver, that is, a receiver in which the pressure changes periodically the resistance of carbon granules. The microphone is supplied not with direct current in the usual way but with alternating current of the same frequency as the sound, from a phase-shifting transformer. Let  $(R_0 + R_1 \sin \omega t)$  represent the microphone resistance, the alternating term representing the effect of the sound falling on it, and let  $i_0 \sin (\omega t + \alpha)$  represent the alternating current supplied to it. The potential difference between its terminals is

$$(R_0 + R_1 \sin \omega t) \times i_0 \sin (\omega t + \alpha),$$

or

$$R_0 i_0 \sin (\omega t + \alpha) - \frac{1}{2} R_1 i_0 \{ \cos (2\omega t + \alpha) - \cos \alpha \},$$

and this has a steady component of  $\frac{1}{2} R_1 i_0 \cos \alpha$ . A direct current galvanometer connected in series with the microphone is therefore deflected by an amount proportional to  $\frac{1}{2} R_1 i_0 \cos \alpha$ . If the phase of the current supplied to the microphone is adjusted to quadrature with the periodic change of microphone resistance,  $\alpha$  becomes  $90^\circ$ ,  $\cos \alpha$  becomes zero and the deflection of the direct current galvanometer is brought to zero. A null method of phase measurement is obtained in which the galvanometer is used to adjust the current supplied to the microphone to quadrature with the periodic change of microphone resistance. It is to be noted that there is a constant phase difference between the sound pressure on the microphone and the periodic change of microphone resistance, depending upon the mechanical constants of the microphone. The changes of phase as the microphone is moved about in the sound field can however be easily and quickly measured.

## § 5. ACKNOWLEDGMENTS

The author desires to express his indebtedness to the Admiralty for permission to publish this paper, and to Mr B. S. Smith for his inception of the microphone phase-measuring device and valuable suggestions and advice concerning the phase-shifting transformer.

\* "The measurement of transmission and reflection of sound by partitions," *Phil. Mag.* 3, 181 (1927).

† "An instrument for the production of known small high frequency alternating electromotive forces," *Proc. Phys. Soc.* 41, 18-28 (1928).

## DISCUSSION

Dr C. V. DRYSDALE: I should like to congratulate the author, as a member of my own scientific staff, on his contribution to a subject of great and growing importance. In spite of the enormous development of acoustics in connection with telephony and sound reproduction, acoustic measurement is still in its infancy, and we are much in the same condition as electrical engineers were before the advent of ammeters and voltmeters. Acoustic vibrations are easily convertible into electrical ones, but the two great difficulties are the extremely small power available and the uncertainty as to the amount of it converted, owing to the reflecting properties of the receiver and the disturbing effect of its presence in the wave-fronts. For these reasons, absolute acoustic measurements are exceptionally difficult, and, although certain methods have been devised which are beautiful in theory, their use is attended with great difficulties and uncertainties. The author's contribution to this problem is certainly a valuable one and does give an absolute measurement of the pressure on the receiver piston, regarded as a rigid surface, by a comparatively simple and accurate method, although a factor of between 1 and 2 must be applied depending upon the ratio of the diameter of the piston to the wave-length of the sound. Care must of course be taken, in cases where the diameter is large, that the receiver face is perpendicular to the direction of propagation, but this merely requires turning it until the e.m.f. is a maximum. As an old worker with phase shifting transformers, I should also like to express appreciation of Messrs B. S. and F. D. Smith's simple and convenient phase shifter, with its device for varying the magnitude as well as the phase of the secondary e.m.f.

Mr A. S. RADFORD: I should like to call the author's attention to the fact that, besides the obstacle effect of the microphone itself, we have errors due to reflection from other obstacles, such as room walls, which cannot be eliminated and are in general greater than those caused by the presence of the microphone. I should be greatly obliged if the author would tell us if his transmitter is intended for use over the whole audible frequency range, or only to measure the distribution of intensity around a source for a single frequency. It would seem that for low frequencies especially this type of microphone would be less sensitive than, say, the condenser transmitter.

Mr W. WEST: The method aims at a measurement of the total alternating force exerted on the piston. The author mentions the desirability of interpreting the results in terms of pressure in the unobstructed sound field. For this purpose it is necessary to stipulate that the sound emanates from a single source, i.e. that measurements are made in open air or the acoustical equivalent, since the presence of reflecting surfaces, in effect, increases the number of sources of sound. For all work where sustained pure tones are to be measured (e.g. in obtaining frequency characteristics of loud speakers), both the calibration and the use of the sound detector should be effected under this condition, otherwise the instrument may fail to give a measure, not only of intensity but also of pressure, with any degree of

accuracy. It is assumed that the piston, together with its attachment to the moving coil, is rigid. There will, I think, be practical difficulties, especially when dealing with the more acute audible frequencies, in the design of a suitable mechanical structure whose effective mass is sufficiently small to permit reasonable sensitivity while its rigidity can be relied upon at such frequencies. I am referring in particular to the measurement of sound in air.

Mr A. J. ALDRIDGE: The method described by the author is really a modification of the Gerlach compensator, but he avoids one of the chief difficulties of the Gerlach method, namely, the determination of the balance point—at any rate in those cases (and they are far the most numerous) where the magnitude of the sound and not its phase is required. The author has deduced a very simple formula to determine the acoustic pressure, but it is always advisable whenever possible to obtain confirmatory results. No information is given as to whether any have been obtained. Dr Drysdale appears rather contemptuous of the other methods of measuring sound. In the Post Office Research Laboratories, Rayleigh discs are in almost daily use for sound measurement and are found entirely satisfactory. They are robust and easily made, calibrated and used. In Germany a modified Gerlach compensator is found very satisfactory, and in America and in the C.C.I. Laboratory in Paris thermophones are in constant use. Good agreement is obtained between calibrations by these various methods, and I would like to ask the author if he has made any comparisons between his method and others, and, if so, with what result?

Dr A. B. WOOD: To those who appreciate the practical difficulties of sound-intensity measurement, the paper will come as a valuable contribution to the subject. In addition to this, it serves as a good example of the modern tendency to develop the theory of mechanical oscillatory systems on electrical lines, a tendency to which the President drew attention in his address to the Society a short time ago. The paper gives us a very simple method of determining the absolute pressure-amplitude in the medium, in the absence of the receiver. Certain limitations are necessarily imposed. In the first place, the wave form must be sinusoidal, for the receiver, regarded as an obstacle, must fulfil certain conditions with respect to its dimensions relative to a wave-length of the sound. A receiver would therefore behave differently as an obstacle towards the higher harmonics and the fundamental. A receiver to deal with complex sounds would on this account have to be large compared with a wave-length of the fundamental, or small compared with the wave-length of the highest harmonic. It is pleasing to note that the author has drawn attention to the relation between the effective pressure and the size of the receiver, a point which hitherto has been entirely overlooked by many writers on the subject. A complex wave form would also introduce additional complications into the electrical method of measurement which is described in the paper. It would appear also that the method, although theoretically applicable to frequencies far removed from the resonant frequency of the receiver, would in practice be inaccurate at such frequencies, owing to the difficulty of measuring very small



values of the motional impedance  $z_m$ . In the introduction to the paper the author refers to the null method of measuring sound intensity by means of the Gerlach strip receiver. I should like to have his opinion regarding the advantages which he claims for his own method over that of Gerlach and Meyer. I conclude by congratulating him on a very nice piece of work. It is to be hoped that he will extend his treatment of the subject to other types of receiver.

**AUTHOR'S reply:** The work described in my paper was carried out with a view to measurements of sound intensity in water. The Rayleigh disc and the condenser microphone recommended by Mr Aldridge for measurements in air are inadequate in water, the former being inconvenient and the latter insensitive. The difficulties which have to be overcome are not the same for the two media. For example, the mass of water associated with a small rigid piston of, say, 3 cm. radius vibrating in an aperture in a rigid plate is 72 gm. and the corresponding mass of air is only 0.0864 gm. As there are in any case 72 gm. of water associated with the piston and moving coil, there is no point in making it light and therefore no difficulty in making it rigid. On the other hand, a piston and moving coil for use in air must be light and rigid, two conflicting requirements not easily satisfied. Mr West will see that in choosing water as the medium, I have escaped this difficulty.

I cannot describe at length the extensive experiments on sound-intensity measurements carried out at the Admiralty Research Laboratory, but at Mr Aldridge's request I have selected one experiment of special interest for a short description. This test, which was suggested by Mr B. S. Smith, will be recognised by electrical engineers as the acoustical equivalent of the Hopkinson test for a pair of similar direct current machines in which one, used as a motor, drives the other, used as a generator. I placed two exactly similar moving-coil instruments, facing each other at a distance of about 12 ft., in a large tank of water, and used one to generate sound and the other to receive it. I measured and calculated the efficiency of the generator, inferred from the results the efficiency of the receiver, and finally calculated the current which should flow in the coil of the receiver when a known current was supplied to the generator. As the measured current in the coil of the receiver agreed closely with the calculated value, it was clearly safe to use the instruments as receivers for sound-intensity measurements. I feel sure that Mr Aldridge will agree that a calibration of this kind is sufficiently exacting and has, moreover, the advantage that it is self-contained. It has an obvious application in the determination of the frequency characteristics of pairs of loud-speakers in air.

The essential difference between my method and that of Gerlach is that I obtain a balance between the effect of a sound pressure and an electromotive force by reducing the current in the moving coil to zero, whereas Gerlach does so by reducing the motion of the moving coil to zero. In reply to Dr A. B. Wood's question as to the relative merits of the two methods, I think it is sometimes more convenient to detect a small electric current rather than a small mechanical vibration. His objection that the motional impedance  $z_m$  is very small at frequencies

remote from resonance can be met by measuring the effective mechanical impedance  $Z$  instead and using formula (8).

Mr Radford and Mr West have emphasised the confusion which arises from the presence of reflecting surfaces in the vicinity of the measuring apparatus. Even in open air and in the sea the reflections from the ground and the surface of the sea are an unmitigated nuisance. The difficulty which is common to all sound-intensity measurements can be partly avoided by the use of directional transmitters and receivers and sound-absorbing materials.

In reply to Mr Radford, the transmitter shown in Fig. 1 is suitable for sonic frequencies in water but not in air. It should be possible to fit a moving-coil loud-speaker with a more rigid piston for use in air and to compensate for the loss of sensitiveness by increased amplification.

# THE MEASUREMENT OF THE VISCOSITY OF GLASS AT HIGH TEMPERATURES BY THE ROTATING CYLINDER VISCOMETER

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Communication from the Staff of the Research Laboratories of the General Electric Company, Limited, Wembley

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**ABSTRACT.** After reviewing previous work on the subject, the paper describes an apparatus in which the molten glass is contained in a cylindrical sillimanite pot provided with a coaxial cylindrical stirrer which is caused to rotate: the viscosity is inferred from the angular velocity produced in the stirrer by a measured torque. The apparatus was calibrated by measurement with it of the viscosities of golden syrup and pitch, these quantities being also measured independently with a falling sphere viscometer and by a torsion method respectively. The calibration factor of the authors' apparatus appears to be independent of the viscosity over a wide range. The authors' results and those of previous workers are considered to be in reasonable agreement with one another when allowance is made for differences in composition of the samples used.

## § 1. INTRODUCTION

THE measurement of the viscosity of glass at high temperatures involves considerable experimental difficulties.

Valuable work has been done by Washburn and Shelton<sup>(1)</sup>, English<sup>(2)</sup>, Stott<sup>(3)</sup>, and Gehlhoff and Thomas<sup>(4)</sup>. As the glasses used by the above workers have not the same chemical composition, a direct comparison of their measurements is not possible. Further difficulty arises in view of the fact that the published compositions of the glasses are not all chemical analyses.

Washburn calculated the composition of his glasses from the known composition of three of them, which were mixed in varying proportions, and even so all the minor constituents were neglected. Gehlhoff and Thomas calculated their glass compositions from the batch formula and this gives rise to some uncertainty. Furthermore, they have published their results in a rather different form, and the scale of the diagrams is so small that additional uncertainty is introduced when the data are read from the curves.

English and Stott give the analysis of the glass actually used.

One or two other points arise in comparing the published data, but these are dealt with later in the paper in the appropriate sections.

An approximate comparison between the results obtained by Washburn, English and Stott has been made by Stott in one case, where the three workers give data for glasses of approximately similar composition. This will be dealt with, in more detail, later.

The lack of agreement shown by Stott's comparison, and the importance of the subject, have encouraged the authors to attempt a further study of the problem.

Washburn, English, and Gehlhoff and Thomas all used viscometers of the concentric cylinders type applying a given torque to the inside cylinder and measuring its speed of rotation, the outside cylinder being rigidly held.

Stott<sup>(5)</sup> measured the viscosity of glass from the founding temperature down to about 1000° C. by determining the rate at which a platinum-iridium sphere attached to the end of a platinum-iridium wire was raised through the glass under a given force.

In a later work <sup>(6)</sup> he determined the viscosity of glass by weighing the quantity of glass carried on a platinum-iridium wire withdrawn at a definite rate from a pot of glass maintained at a constant temperature, utilising the principle developed by Goucher and Ward <sup>(7)</sup> at these Laboratories for the coating of fine wires with various suspensions.

As previously mentioned, an approximate comparison between the results of English, Stott and Washburn has been made by Stott<sup>(8)</sup> for glasses of approximately similar compositions. His results are reproduced in Fig. 1.

The curves represent the results of the three workers on glasses of the compositions shown in Table I.

Table 1. Analyses of the glasses compared by Stott

	Stott, N.P.L. 15	English, No. 6	Washburn
SiO <sub>2</sub>	72.22	73.18	72.22
Al <sub>2</sub> O <sub>3</sub>	0.71	0.58	—
Fe <sub>2</sub> O <sub>3</sub>	0.11	0.61	—
CaO	6.94	6.26	8.29
MgO	0.53	0.21	—
Na <sub>2</sub> O	19.49	19.38	19.49

The curve marked "English" was obtained by Stott from English's figures for his glass No. 6 after applying a small correction, derived from Washburn's isokoms, to allow for the slight differences in composition. In the making of this adjustment, the corrections were calculated from the percentages of soda and silica only. The circles slightly above the curve are English's actual points. Washburn's curve was derived from his isokoms.

From Fig. 1 it is seen that whilst the curves of English and Stott are approximately parallel at the lower temperatures, they diverge considerably at the higher temperatures, English's curve becoming much flatter than Stott's. It is also noticed that Washburn's curve has a much steeper slope than either of the other two.

In calculating the viscosity from his measurements, Washburn used a calibration factor which varied over a wide range (approximately 3 to 1) with the viscosity,

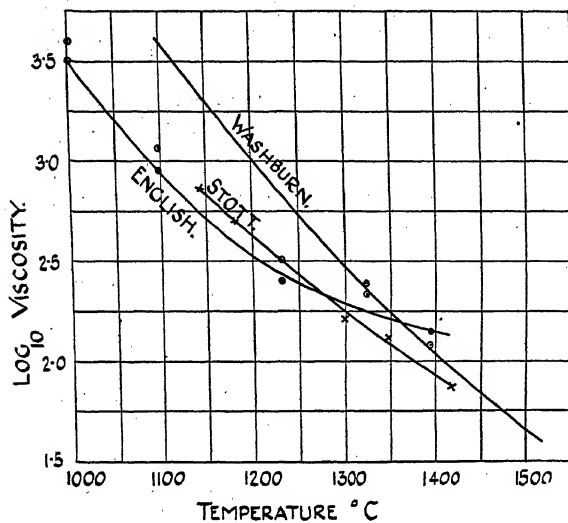


Fig. 1. Comparison of viscosity data obtained by various workers (extracted from paper by Stott, *Journ. Soc. Glass Tech.* 9, 207 (1925)).

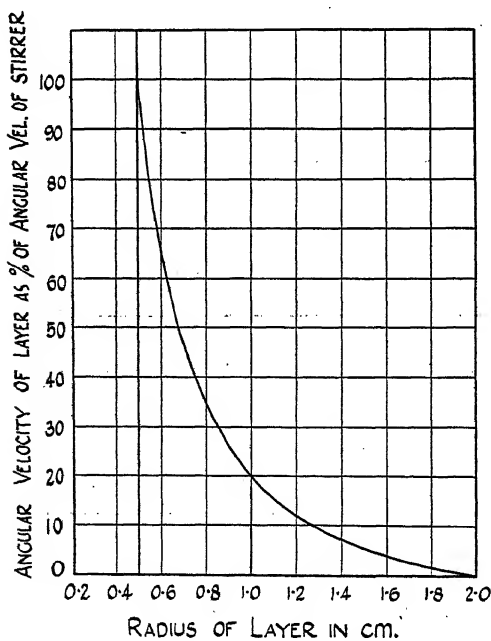


Fig. 3. Diagram showing distribution of angular velocity of the liquid in viscometer.

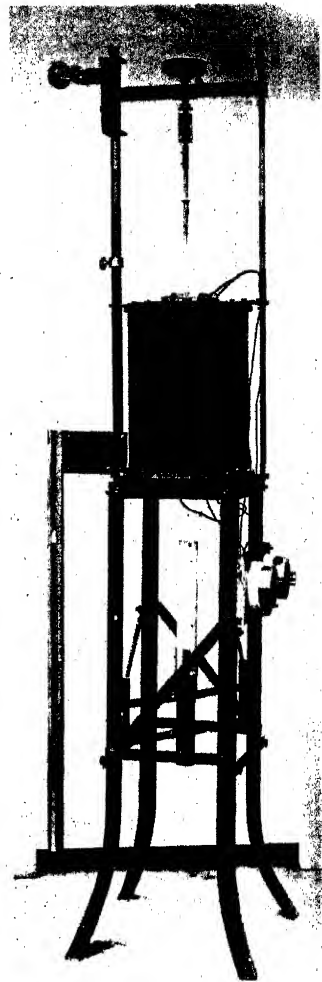


Fig. 2. Rotating cylinder viscometer.

in a manner which he had previously determined by calibration with liquids of different viscosities.

If a constant factor is used (as suggested by Stott) in calculating the viscosity from Washburn's results, a curve is obtained which has approximately the same slope as that of the other two workers. Later in the paper a constant factor is deduced for Washburn's apparatus based on the authors' experience and the agreement between his results and those of others is improved. A constant factor was employed by English in his measurements. He, however, only calibrated his apparatus at low viscosity values and apparently assumed a constant factor over the whole range.

Whilst the wire method which has been developed so successfully by Stott is ingenious, the calculation of the viscosity from its results involves a knowledge of the surface tension and the authors decided to devote their attention to the rotating cylinder method.

## § 2. DESCRIPTION OF APPARATUS

The general details of the apparatus are shown in Fig. 2. The stirrer has been raised from the furnace and the pillar which supports the pot lowered. For the sake of clearness, the pot has been removed from its position on the pillar and has been placed on the top of the furnace.

The furnace is heated by means of eight silit rods arranged concentrically round the pot. The upper ends of these rods can be seen in the figure. By means of switches it is possible to connect the rods in various series—parallel arrangements; so that a large range of temperature can be covered with the aid of a comparatively small external resistance.

The glass under test is contained in the sillimanite pot which is 4.0 cm. in internal diameter and about 5.5 cm. deep. The pot is kept from revolving by means of a cross, moulded on the bottom of it, which fits into a corresponding recess on the top of the sillimanite pillar. The pillar is clamped in guides and can be raised or lowered as desired.

The stirrer, which is also composed of hard-burnt sillimanite, is made from a bar  $12 \times \frac{1}{2} \times \frac{1}{2}$  in., the lower 3 in. of which are accurately ground to  $0.97 \pm 0.005$  cm. The upper portion of the stirrer is roughly ground to fit the mild-steel sleeve and is prevented from turning in it by means of set-screws which engage a groove in the stirrer. The sleeve is clamped in a brass chuck, screwed on to the lower end of a bicycle axle, and can be centred so that the lower end of the stirrer rotates truly about its axis.

The upper end of the axle is attached to a light pulley wheel about 11 cm. diameter. The torque is applied by means of a known weight hung on the end of a fine wire attached to the circumference of the pulley.

By means of set-screws pressing against the circumference of the lower end of the furnace, it is possible to adjust the stirrer so that it is concentric with the pot.

In order to close the top of the furnace as effectively as possible and divert any convection currents away from the main body of the stirrer, a small sillimanite

collar is slipped over the stirrer, its height being such that it just clears the under side of the furnace cover. The bottom of the furnace is closed by means of a piece of asbestos cord wrapped around the pillar at the point where it leaves the furnace.

Initially the temperature of the glass was measured by a chromel-alumel thermo-couple arranged in contact with the under side of the pot or its outside edge. However, during the early stages of the measurements it was found that greater accuracy could be obtained by imbedding the couple in the stirrer. Owing to the small diameter of the stirrer, the method adopted is to insert the couple in two holes, moulded throughout the length of the stirrer and connected by a slot at the bottom end. After the insertion of the couple, the slot is cemented up and baked, and the couple is calibrated against a platinum, platinum-rhodium couple which had been previously calibrated against melting points. To allow the stirrer to revolve freely, the thermo-couple is stopped short just outside the top of the stirrer. When it is desired to take a reading, the couple is extended by pieces of the same wires, so that the cold junction is placed in a convenient position. Control of the temperature of the glass is facilitated by the introduction of another couple outside the pot, which is under continuous observation.

The best position for the pot in the furnace was determined experimentally as follows. A pot was filled with glass and the apparatus adjusted in readiness for a test. A fine thermo-couple having a thin silica sheath was then immersed in the glass and the temperature measured at various points, the results being compared with that recorded by the stirrer couple. This was repeated with the pot and stirrer raised or lowered until the most concordant results were obtained. In this position with the furnace temperature at  $1000^{\circ}\text{C.}$ , the glass in the neighbourhood of the stirrer was at the same temperature as the stirrer and the glass remote from it differed on the average by  $2^{\circ}$ , the maximum difference at the ends of the pot being  $5^{\circ}$ . The differences are less at the lower temperatures. As will be seen later, the rate of change of the angular velocity of the glass increases from the walls to the stirrer. If, therefore, the temperature distribution is not rigidly constant, it is better to measure the temperature at the stirrer rather than at the walls of the pot.

### § 3. DISCUSSION OF ERRORS

Before the calibration of the apparatus was commenced, the effect of errors in measured quantities on the precision of the measurements was determined.

The factors considered were:

- (1) Measurement of temperature.
- (2) Diameter of pot.
- (3) Diameter of stirrer.
- (4) Height of liquid in pot.
- (5) Friction of rotating system.
- (6) Depth of immersion of stirrer.
- (7) Eccentricity of stirrer.
- (8) Deviation of axis of rotation from axis of stirrer.
- (9) Load.
- (10) Speed of rotation.

(1) *Temperature measurement.* In the case of concentric cylinders, where the outer cylinder is stationary, it can be deduced theoretically that, neglecting friction and end corrections,

$$\eta = K M / \phi_o$$

$$\text{where } K = (gR/8\pi^2 l) (1/r_i^2 - 1/r_o^2) \quad \dots\dots(1).$$

$\eta$  is the viscosity in c.g.s. units,

$M$  the load on the wire,

$R$  the radius of the pulley,

$l$  the length of the cylinders,

$r_o$  the radius of the outside cylinder,

$r_i$  the radius of the inside cylinder, and

$\phi_o$  the revolutions per second of the inner cylinder.

It follows that

$$\phi = (MgR/8\pi^2 l \eta) (1/r^2 - 1/r_o^2) \quad \dots\dots(2)$$

where  $\phi$  is the angular velocity at radius  $r$ .

Fig. 3 gives the velocity of the liquid at any point between the cylinders as a percentage of that of the inner cylinder, calculated by means of Equation (2), for cylinders having radii approximately equal to those of the pot and stirrer respectively. It is seen that, in this case, the velocity of the liquid at a distance of 0.1 cm. from the stirrer is about 32 per cent. less than that of the stirrer, whereas the change in velocity over a corresponding distance adjacent to the walls of the pot is less than 1 per cent.

From this it is clear that, for a given change in  $\eta$ , the change produced in  $\phi_o$  is much greater for small values of  $r$  than for large. This point can also be demonstrated by differentiating Equation (2) with respect to  $r$ . For accurate working, therefore, it is more important to measure correctly the temperature of the layers adjacent to the stirrer than to measure correctly the mean temperature of the glass wherever the temperature is not rigidly constant.

The temperature determined by the couple in the stirrer is considered to be within  $\pm 2^\circ$  of the true temperature at  $1000^\circ \text{C}$ .

(2) *Diameter of pot.* For a reason similar to that discussed in the previous section, small variations of the order of 0.05 cm. in the diameter of the pot do not appreciably affect the viscosity measurements.

(3) *Diameter of stirrer.* An examination of the curve given in Fig. 3 shows that an error of 0.005 cm. in the diameter of the stirrers (which represents the limit of accuracy of the stirrers) produces an error of about 1 per cent. in the measurements.

(4) *Height of liquid in pot.* Similarly Equation (1) shows that an error of 0.02 cm. in the measurement of the height of the liquid in the pot introduces an error of about  $\frac{1}{2}$  per cent. into the viscosity measurements. As Equation (1) does not take into account the end effects, it is probable that the actual error produced by the above difference in height is somewhat less than this amount. (Since the apparatus is calibrated against liquids of known absolute viscosity, the actual end correction does not matter.)



(5) *Friction of rotating system.* This was determined over a wide range of velocities with the stirrer rotating in air. It was found that whilst the friction varied from day to day, the value of the load equivalent to the friction lay between 1.5 to 1.8 gm. weight and there was no appreciable variation with speed.

(6), (7) and (8). *Errors due to changes in the relative positions of stirrer and pot.* To determine the magnitude of the errors due to causes (6), (7) and (8), a series of tests was made with Lyle's golden syrup. For these tests the sillimanite stirrer and pot were replaced by a brass tube and pot respectively, and in order to improve the accuracy of the temperature measurements, they were raised out of the furnace

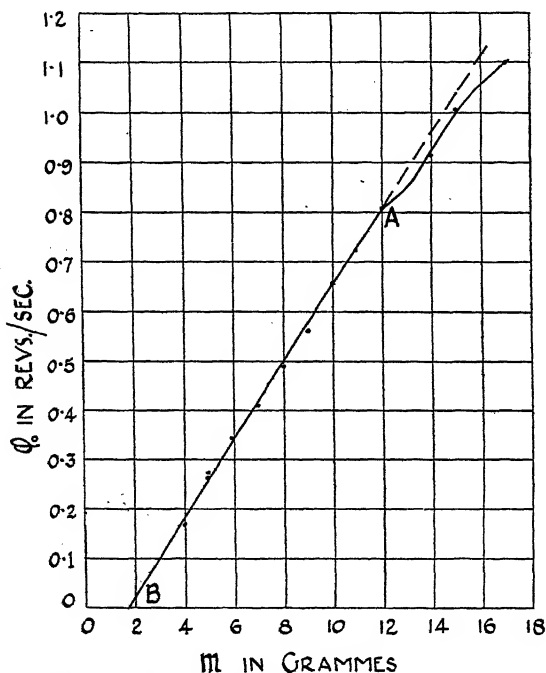


Fig. 4. Diagram showing relation between angular velocity of stirrer and applied load.

and surrounded by a water jacket. The temperature was measured by a thermocouple placed inside the stirrer, which contained a little glycerine to improve the thermal contact. The temperature was maintained constant to within  $0.1^{\circ}\text{C}$ .

With the stirrer raised, the pot was filled with syrup to a depth of 5.0 cm. The stirrer was next lowered to the bottom of the pot and then raised 0.5 cm. Before readings were taken one complete revolution was allowed to ensure of the stirrer attaining a uniform velocity. This was found to give sufficient time for the stirrer to reach approximately uniform motion.

In making the measurements the time of three complete revolutions was taken for various loads and the revolutions per second calculated. The results of a typical test are shown in Fig. 4.

When the angular velocity of the stirrer exceeded a certain definite value turbulent motion set in, as is seen by the departure from the linear relation between  $M$  and  $\phi_0$  at  $A$ . It is of interest to note also that the intercept on the load axis is 1.7 gm. weight corresponding to the friction as determined in air. In all viscosity determinations the slope of the straight portion  $AB$  corresponding to purely viscous flow was used in the calculations. Experiments were made for a number of relative positions of pot, stirrer and axis of rotation. The results are given in Table 2, where errors in viscosity due to various errors in adjustment are given for these experiments.

Table 2. Errors in viscosity due to variations in adjustment of apparatus

Adjustment	% change in $M$ /revs. per sec. due to 0.1 cm. variation in adjustment	Accuracy of adjustment in cm.	% error in final result due to error of col. 3.
(1)	(2)	(3)	(4)
Distance of stirrer from bottom of pot	2.6	0.02	0.5
Eccentricity of stirrer and pot	0.9	0.02	0.2
Eccentricity of stirrer from axis of rotation	1.3	0.015	0.2

(9) *Load*. The load could be determined to as high an accuracy as desired.

(10) *Speed of rotation*. At the higher speeds the accuracy of an individual measurement was about 1 per cent., but to improve this more repeat observations were made at the higher than at the lower speeds.

#### § 4. CALIBRATION OF APPARATUS

For the calibration of the apparatus at low viscosities (about  $10^3$  c.g.s. units) Lyle's golden syrup was employed. To determine the viscosity of the syrup a falling sphere viscometer of the following dimensions was employed:

Length of tube	40.3 cm.
Radius of tube	1.125 cm.
Radius of sphere	0.0793 cm. (1/16 in. Hoffman ball.)

The viscosity was calculated from the rate of fall of the sphere through the central portion of the column by means of the Ladenburg formula (9), viz.:

$$9\eta V(1 + 2.4x)(1 + 3.3 r/h) = 2gr^2(s - \sigma),$$

where  $V$  is the velocity of sphere,

$\eta$  the viscosity,

$x$  the radius of the sphere ( $r$ ) divided by the radius of the vessel,

$h$  the height of liquid in vessel,

$s$  the density of the sphere, and

$\sigma$  the density of the liquid.

In calibrating the rotating cylinder apparatus with the syrup, the following procedure was adopted. The viscosity of a portion of the syrup was first measured over a range of a few degrees, at a suitable temperature, by means of the falling sphere viscometer. The centre portion of the column of syrup was then transferred to the pot and a series of measurements of load and revolutions per second was taken in the rotating cylinder apparatus as soon afterwards as the steadying up of the temperature of the syrup would allow. To increase the accuracy of the determination of  $\phi_0$  (the revolutions per second) three revolutions were allowed to pass, the time for the twelve subsequent revolutions was measured, and this measurement was repeated on several occasions. During both of the determinations the temperature of the syrup was kept steady to within  $0.1^\circ \text{C}$ . (approximately). The calibration factor ( $K$  in Equation (1)) for the apparatus was then determined from the viscosity of the syrup and the slope of the load/revolutions-per-second curve.

Five independent calibrations were made, a fresh portion of syrup being used each time. To eliminate any possibility of error due to variation of the viscosity of the syrup owing either to time or to lack of homogeneity, a separate determination of the viscosity by the falling sphere method was made for each calibration.

The results of the five calibrations are shown in Table 3.

Table 3. Calibration factor determined with syrup

Viscosity c.g.s. units	$K$	Mean $K$	% variation from mean
523.6	52.2	53.4	- 2.3
203.0	54.6		+ 2.2
264.9	53.7		+ 0.64
478.6	53.2		- 0.32
337.3	53.3		- 0.13

For calibrating the apparatus at high viscosity values, pitch was employed. As it was not convenient to use the falling sphere viscometer owing to the high viscosity necessitating long periods of time, and the opacity of the pitch requiring the use of X-rays, it was decided to determine its viscosity by means of torsion.

Rods about 20 cm. long by 1.3 cm. in diameter were made by rolling the pitch between two flat boards, in a manner similar to that described by Trouton and Andrews<sup>(10)</sup>, and square tapered ends were pressed on to them by means of the brass cups (see Fig. 5).

The lower brass cup was clamped to the top of the furnace to prevent it from rotating, whilst the upper cup was mounted in the chuck of the stirring gear. A bath containing a solution of calcium chloride was fixed around the pitch rod to prevent it thinning down at the top owing to viscous flow under gravity. By means of an electric heater the bath could be kept at any desired temperature.

To eliminate any errors due to twisting of the ends of the rod, the following procedure was adopted. In essentials it is similar to that used by Stott<sup>(5)</sup> in his low-temperature viscosity measurements. A fine line was made down one side of the rod and the diameter of the rod was measured in several places. The rod was

then mounted in place and the temperature steadied. After the temperature had been steady for about 20 minutes a set of readings of time and distance through which the weight had fallen was recorded for a given load. A typical set of observations is shown in Fig. 6. (As the circumference of the pulley wheel is 34.5 cm., one revolution of the stirrer corresponds to 34.5 cm. fall of the weight.) At the end of the test the mean distance between consecutive turns of the helix was measured by means of a pair of sliding calipers. The rod was then taken out and remeasured. The rod was replaced in the apparatus, the pitch of the helix was measured and a second test was carried out with a different load. As before, after a series of readings of time and distance traversed by the weight had been taken, the new mean pitch

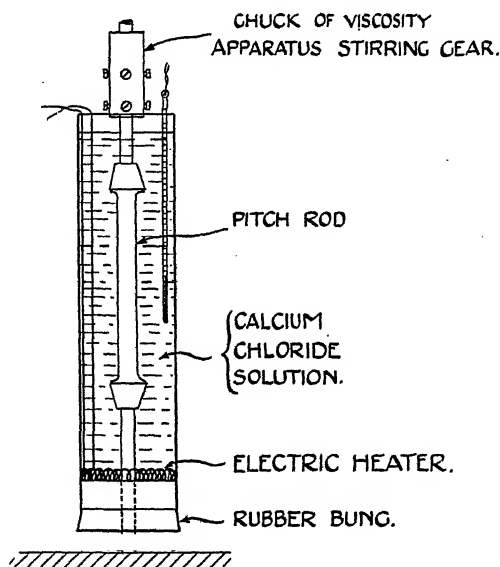


Fig. 5. Supplementary apparatus for measuring viscosity of pitch by torsion.

of the helix was measured. In this manner it was found possible to utilise the same rod for three or four tests. The minimum pitch used was 2.5 cm. which could be measured to within 0.025 cm., i.e. 1 per cent.

It can be shown theoretically that

$$\eta = 2MgR/\pi\omega r^4 = (2Rg/\pi r^4) M/\omega \quad \dots\dots(3),$$

where  $M$  is the load,

$R$  the radius of the pulley,

$r$  the radius of the pitch rod,

$\omega$  the angular velocity of twist of rod per unit length, viz.  $2\pi/pt_0$ ,

$p$  the mean pitch of helix, and

$t_0$  the time of test corrected for plastic flow.

The value of  $t_0$  is determined as follows. Referring to Fig. 6,

$$t_0 = OD \times AD/AB = t \times AD/AB.$$

The mean pitch corresponding to any one test was calculated from the initial and final pitches by means of the equation

$$p = p_o p_i / (p_o - p_i)$$

where

$p_o$  is the initial pitch of the helix and  
 $p_i$  the final pitch of the helix.

From the measurements of the pitch of the helix and from the time-scale-reading curves for various loads, similar to Fig. 6, the straight lines in Fig. 7 showing the change of  $\omega$  with  $M$  have been calculated.

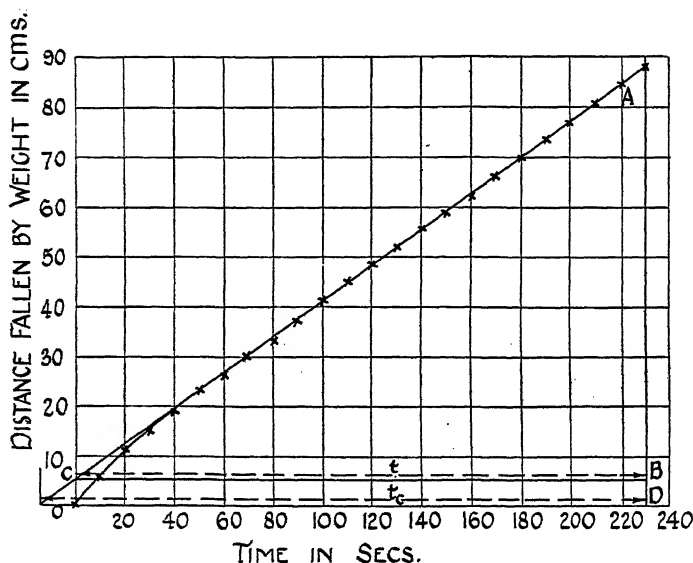


Fig. 6. Diagram showing relation between the twist and time for pitch rods subjected to torsion.

Substituting the values for the slope of these lines in Equation (3), we obtain for the viscosity of the pitch the results shown in Table 4. These results have been plotted in Fig. 8.

Table 4. Viscosity of pitch

Temp. ° C.	Viscosity in c.g.s. units	Log <sub>10</sub> viscosity
23.0	$1.906 \times 10^8$	8.281
23.6	$1.557 \times 10^8$	8.193
25.0	$0.987 \times 10^8$	7.994
25.9	$0.904 \times 10^8$	7.954
26.9	$0.683 \times 10^8$	7.834

Half of the rods used in the torsion measurements were then melted into the pot of the rotating cylinder viscometer, only sufficient heat to let the pitch gradually settle down in the pot being used. After the temperature had been steady for about

30 minutes, the speed of rotation of the stirrer was determined for loads of 200, 300, 500, 1000, 1500 and 2000 gm. weight. The results are shown in Fig. 9.

Referring to Fig. 8 and Equation (i), we obtain  $K = 52.4$ .

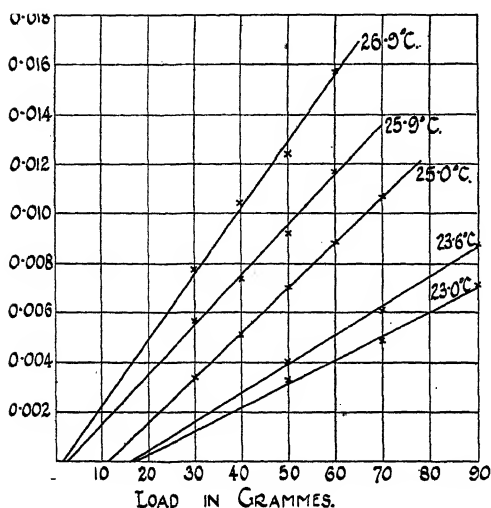


Fig. 7. Diagram showing the relation between twist and ad for pitch rods under torsion at various temperatures.

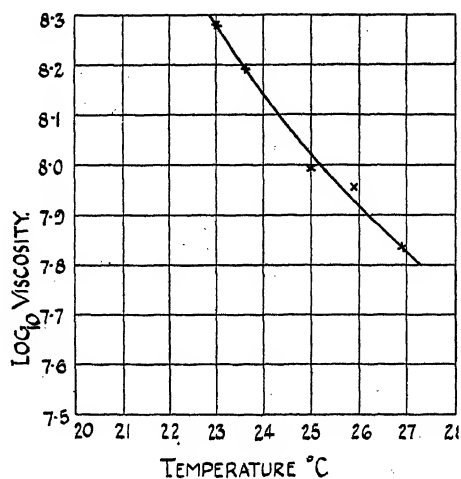


Fig. 8. Diagram showing viscosity-temperature relation for pitch.

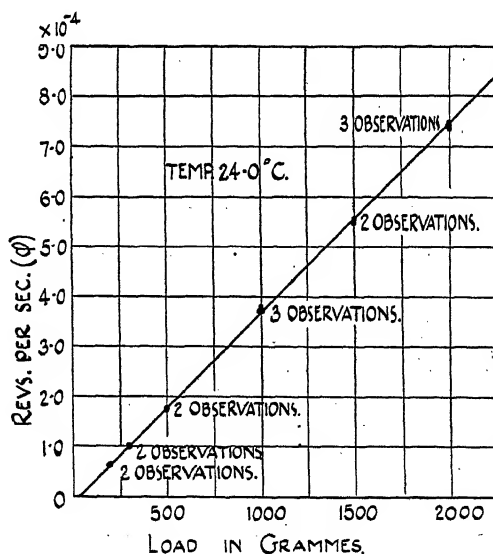


Fig. 9. Diagram showing relation between angular velocity and load for pitch.

A repeat test made with the remaining half of the rods gave  $K = 51.5$ .

The mean result is 52.0, which is 3 per cent. lower than the constant calculated from experiments with syrup.

As the determination of the calibration factor, when pitch having a viscosity of about  $10^8$  c.g.s. units is used, agrees with the value obtained with syrup at a viscosity of  $10^3$  c.g.s. units, within the limits of accuracy of the present measurements, it was felt that determinations of the calibration factor at intermediate viscosities was unnecessary.

Further, the calibration constant adopted for subsequent work is 53.0, a value approximating nearer to that obtained when using syrup. This value, the authors feel, is justified in view of the greater inherent difficulty in determining the viscosity of the pitch.

#### § 5. DISCUSSION OF RESULTS

From the foregoing results it appears that, contrary to Washburn's experience, the calibration factor for a rotating cylinder viscometer is independent of the viscosity, over the range  $10^3$  to  $10^8$  c.g.s. units at any rate. As Washburn's calibration factor was the result of a direct calibration over the whole range of viscosity covered by his measurements, it is desirable to seek for an explanation of the large variation he obtained in the value of his factor with viscosity.

A possible explanation was suggested to the authors as the result of some viscosity measurements made on a sodium silicate solution. When they commenced the present measurements they had intended to use sodium silicate as a calibrating medium in place of syrup owing to its higher viscosity. It was found, however, impossible in this case to obtain concordant figures for the calibration factor of the rotating cylinder viscometer, the results of four successive calibrations being

63.0, 64.8, 67.1, 84.0,

a variation of over 30 per cent. The results obtained by the falling sphere viscometer did not show any marked change in the viscosity of the sodium silicate. The large changes above noted were attributed to the development of a skin on the sodium silicate.

When the stirrer was immersed into the pot, it would carry this skin part of the way down with it, a portion only of the stirrer piercing the skin. The effect of this would be to create a thin air film round the upper portion of the stirrer and thus reduce its effective length. This would cause the stirrer to revolve faster, for a given torque, than it would if its whole length were in contact with the liquid, resulting in a high value for the calibration factor. The skin was found to be more pronounced and more troublesome as the calibration work proceeded, and probably this accounted for the ascending magnitude of the factor.

The calibration curve obtained by Washburn for his apparatus is reproduced in Fig. 10, where 1, 2, 3, 4, 5, 6 refer to his various calibration glasses. Glasses 1, 2, 3, 4 were made from confectioner's glucose with various percentages of water, whilst 5 and 6 had a small percentage of dextrose added. It is stated that glasses 3 and 4 both developed a skin very rapidly; this was very tough in the case of 4. Although it is not stated, it is very probable that 5 and 6 also had troublesome skins on them.

As the values of the viscosity of the glass determined by at least two different methods agree reasonably amongst themselves, it is probable that there is no serious error in them. The authors' experience with sodium silicate suggests that skins on Washburn's glasses produced errors similar to those mentioned above. This suggested conclusion is supported by the fact that glass 4, which Washburn states to have had a very tough skin, gave a particularly high value for the calibration factor. The authors have accordingly drawn the best straight line, yielding a constant calibration factor, through the values obtained for glasses 1 and 2 which were apparently the only ones practically free from a skin. This is shown as a broken line in Fig. 10, and the authors have used it in adjusting Washburn's results before comparing them with their own measurements and those of the other workers.

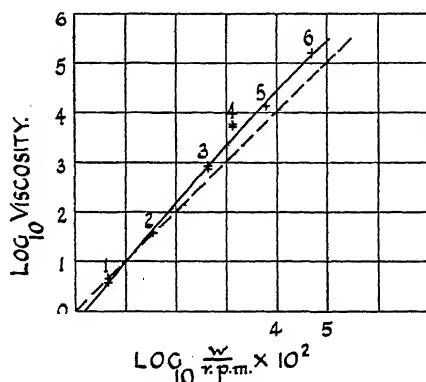


Fig. 10. Diagram showing Washburn's calibration data for his viscometer.

## § 6. MEASUREMENT OF THE VISCOSITY OF GLASS

In conclusion, the authors give the results of viscosity measurements on a glass (C) having a composition similar to those used by others (see Table 5), and following the lines of the previous discussion they attempt to compare the observations with those already published.

Table 5. Viscosity data for Author's glasses

Glass A		Glass B		Glass C	
Temp. ° C.	Log <sub>10</sub> viscosity	Temp. ° C.	Log <sub>10</sub> viscosity	Temp. ° C.	Log <sub>10</sub> viscosity
577	8.820	755	5.924	600	9.812
661	7.337	810	5.339	692	7.444
755	5.995	834	5.133	780	5.906
854	4.977	890	4.689	844	5.182
927	4.389	927	4.519	920	4.345
1048	3.616	932	4.457	953	4.131
1152	3.237	1034	3.725	968	3.965
		1113	3.312	983	3.933
		1182	2.978	1008	3.789
				1055	3.368
				1168	2.822



The accuracy of their determinations for glass is not quite as high as that for the syrup owing to increased difficulty in adjusting the apparatus at high temperatures. It is considered, however, that the errors in the viscosity measurements due to all sources are less than about 6 per cent. at 1200° C. and 10 per cent. at 700° C.

It is interesting to note that the authors experienced a reduction in the accuracy of their results round about 950–1000° C. similar to those experienced by Stott. They hope to investigate this effect further in future work.

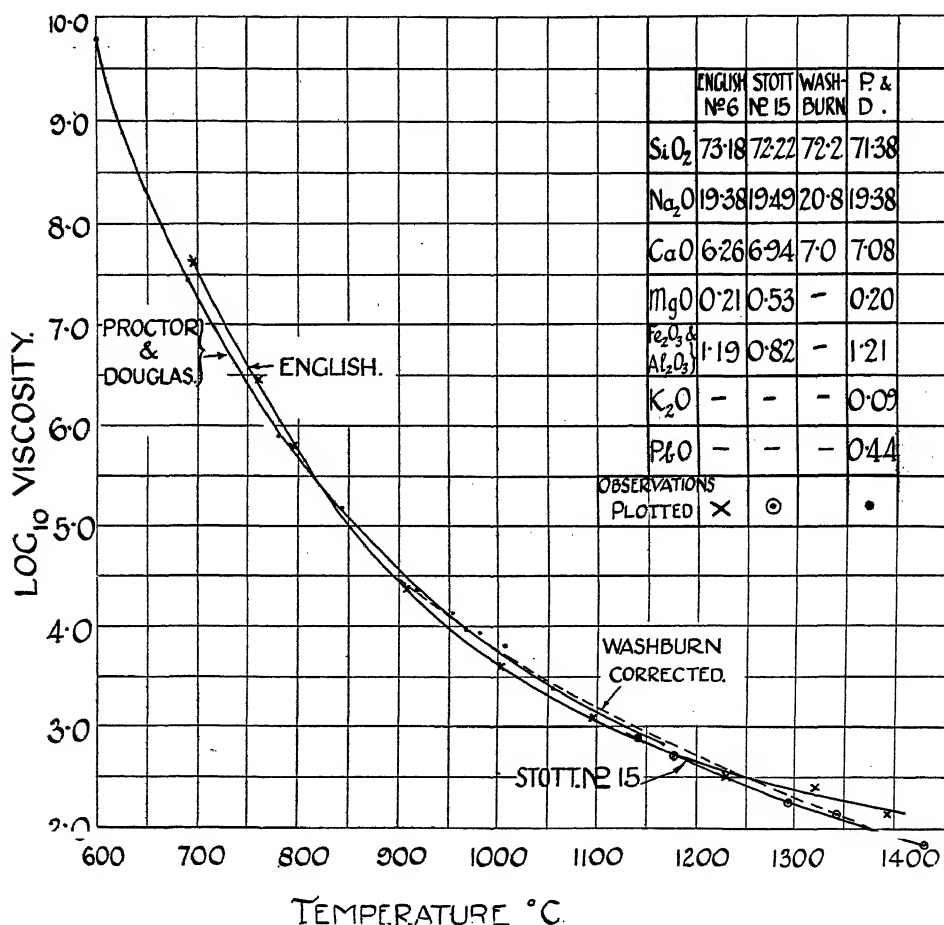


Fig. 11. Authors' comparison of viscosity data by different workers.

In Fig. 11 have been plotted the viscosity results of English, Stott, Washburn, and the authors on glasses of the composition shown in Table 6.

As already noted in the introduction to this paper, the glasses used by Washburn were made by mixing three known glasses in various proportions, the compositions being calculated from analyses of the three parent glasses. In the calculation the impurities were apparently neglected. From an examination of analyses of two of his glasses it would appear that his calculated values for  $\text{SiO}_2$  and  $\text{CaO}$

Table 6. Analyses of glasses compared in Fig. 11

	English, No. 6	Stott, N.P.L. 15	Washburn (from isokoms)	Proctor and Douglas
SiO <sub>2</sub>	73.18	72.22	72.2	71.38
Na <sub>2</sub> O	19.38	19.49	20.8	19.38
CaO	6.26	6.94	7.0	7.08
MgO	0.21	0.53	—	0.20
Fe <sub>2</sub> O <sub>3</sub> and Al <sub>2</sub> O <sub>3</sub>	1.19	0.82	—	1.21
K <sub>2</sub> O	—	—	—	0.09
PbO	—	—	—	0.44

are much closer to the actual values than that for Na<sub>2</sub>O. In view of this, it was decided to fix his glass from a consideration of the percentages of SiO<sub>2</sub> and CaO only. As Washburn's isokoms only make a small angle with the line of constant SiO<sub>2</sub> in his triangular diagrams, for a glass of the above composition, small differences in Na<sub>2</sub>O and CaO do not appreciably affect his results. It will be seen that the correction applied to Washburn's results brings them within 25 per cent. of

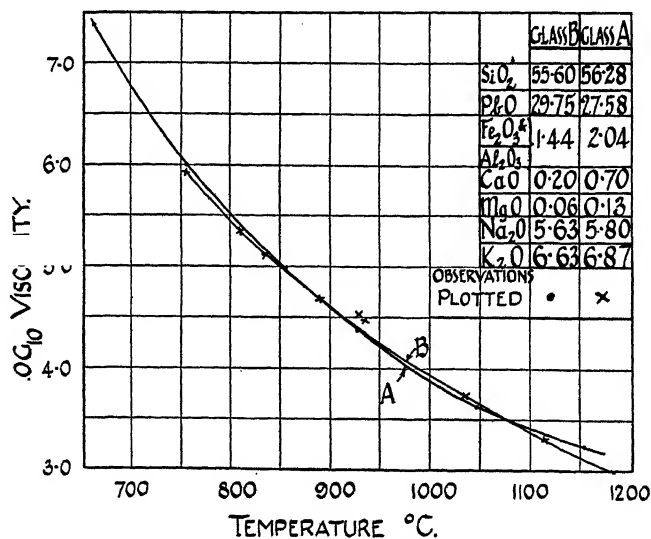


Fig. 12. Diagram showing temperature viscosity curves for two lead glasses differing slightly in composition.

Stott's values over the whole temperature range, and the results obtained by the authors are also practically in agreement with Washburn's, indicating that his glass approximated quite closely to those used by Stott and the authors and that the figure for alkali content probably includes the minor constituents.

In considering English's data, the authors desire to point out that the glass used by him differs quite appreciably from that used by them and has also the lowest lime content of any of the glasses. Stott criticised English's data for the higher temperatures. In a short note written by English as a contribution to a discussion

on viscosity, he makes reference to this and suggests a value of  $10^3$  as a lower limit for his apparatus, in view of small errors in his frictional constant appreciably affecting the results. The authors agree that it is possible for errors from this cause, together with errors due to the inertia of the stirring apparatus, to affect the values of viscosity in this range.

However, the differences in composition cannot be ignored, and in order to emphasise the effect of small changes in composition the compositions and viscosity data for two lead glasses are given in Fig. 12 (and Table 5), whence it will be seen that the differences between the viscosity/temperature curves for these glasses are similar in character to the differences between the curves given by English and the present authors.

It appears, therefore, that all the published data (including Washburn's as corrected by the authors) are in reasonable agreement when allowance is made for the variations in composition.

#### § 7. ACKNOWLEDGMENT

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#### REFERENCES

- (1) E. W. WASHBURN and G. R. SHELTON. *Engineering Experimental Station, University of Illinois, Bulletin* No. 140.
- (2) S. ENGLISH. *Journ. Soc. Glass Tech.* 8, 205 (1924).
- (3) V. STOTT. See (5), (6), (8).
- (4) G. GEHLHOFF and M. THOMAS. *Zeits. für Tech. Physik.* 7, 260 (1926).
- (5) V. STOTT, E. IRVINE and D. TURNER. *Proc. Roy. Soc. A*, 108, 154 (1925).
- (6) V. STOTT, D. TURNER and H. A. SLOMAN. *Proc. Roy. Soc. A*, 112, 499 (1926).
- (7) F. S. GOUCHER and H. WARD. *Phil. Mag.* 44, 1002 (1922).
- (8) V. STOTT. *Journ. Soc. Glass Tech.* 9, 207 (1925).
- (9) W. H. GIBSON and L. A. JACOBS. *Journ. Chem. Soc.* 117, Trans. 1, 473 (1920).  
R. LADENBURG. *Ann. d. Physik.* 23, 456 (1907).
- (10) T. TROUTON and E. S. ANDREWS. *Phil. Mag.* 7, 347 (1904).
- (11) S. ENGLISH. *Journ. Soc. Glass Tech.* 12, 106 (1928).

#### DISCUSSION

Mr C. C. PATERSON: As Director of the Laboratories I should like to offer a hearty welcome to the members of the Physical Society and the Society of Glass Technology.

Mr Proctor has given an account of experiments showing that it is possible to measure, fairly easily and in absolute units, the viscosity of glass over the range at which founding and working takes place. I should like to emphasise how important it is to know and control the viscosity of glass under modern manufacturing conditions. Automatic machine production of glass articles means working the material at as high a speed as possible. The flow of the glass under these conditions

must be uniform for the temperature fixed for the operation, otherwise the processes will be thrown out of gear. I would invite members to study this factor in the bulb-making machines in the glass works you will be visiting, and also in the lamp-making operations.

Mr Dudding has asked me, on behalf of my colleagues here, to invite those members of the Society of Glass Technology who control similar factory operations and who have accurate repeat analyses of their glass, to send us samples which we can test in this viscosity apparatus over the working range. We should be pleased to give them the results, and we think that a comparison, under identical conditions, of a number of glasses of different but well established composition, will be of value to all of us who are seeking to prescribe the best conditions for industrial glass manipulation.

Dr S. ENGLISH: I have been very interested in the paper for both personal and technical reasons. Perhaps I may be permitted to mention the personal reasons first. In 1924 there appeared almost simultaneously two fairly comprehensive papers on the viscosity of glass up to and in some cases beyond  $1400^{\circ}\text{C.}$ ; one was by myself and the other by Prof. Washburn and Mr Shelton. Unfortunately, when dealing with glasses of somewhat similar composition, there was not that concordance in the results that could have been desired. At intervals, since that time, these two sets of data have been reviewed by various workers who seem to have emphasised whatever divergence there was, with the result that confidence in both pieces of work may have been undermined. I am therefore pleased that the authors have so thoroughly investigated the many problems in this very difficult measurement, and that as a result of their work they have been able to confirm my own results and also discover the cause for the divergence between the data given in my paper of 1924 (part II) and those given by Washburn and Shelton. Regarding the curves reproduced in Fig. 1, I thought that I had been able to explain the difference between the curves marked "English" and "Stott"\* and to show that this difference was accounted for by difference in composition, but I am glad to have the corroboration of Messrs Proctor and Douglas in this matter also.

Turning to the technical side, as one who knows the difficulties to be overcome in this particular branch of research, I should like to congratulate the authors on the thoroughness with which they have investigated sources of error, and the care they have taken to ensure accuracy. I have, however, one criticism to make. I consider that, in spite of its cost, the use of a platinum iridium sheath as the inner rotating cylinder is well worth while when dealing with non-lead glasses. Its diameter and surface remain constant for every determination, and its introduction into the molten glass does not give rise to bubbles such as occur whenever a new clay, or sillimanite stirrer is used. A new stirrer of this type is necessary for each determination.

There is one question not mentioned by Mr Proctor in the presentation of this paper which I should like to ask him. In May of last year†, when reviewing

\* *Journ. Soc. Glass Tech.* 10, 32 (1926).

† *Ibid.* 12, 106 (1928).

critically the methods of measuring the viscosity of glass, I suggested that, owing to frictional corrections becoming relatively large when the viscosity of the glass was small, this rotating cylinder method is liable to lose its accuracy when the viscosity of the glass is less than  $10^3$  c.g.s. units. I should be glad to hear whether the authors agree with this suggested useful limit for viscosity apparatus of this type.

MR V. H. STOTT: I wish to congratulate the authors on their very interesting work achieved in the face of considerable experimental difficulties. Unfortunately, I have only just received a copy of the paper, but it has occurred to me that there are two main objects in measuring the viscosity of glass. In the first place, an absolute measurement of viscosity may be desired, or, on the other hand, it may be wished merely to have a sensitive means of checking the variations of viscosity for works control. For the former purpose an apparatus on the lines of that used by the authors is probably the most convenient. It has, however, the disadvantage of permitting a gradual contamination of the glass owing to the solution of the refractory materials in contact with it. Perhaps the authors could tell me whether they experienced trouble of this kind.

Having in mind the second purpose, we have used, in the National Physical Laboratory, an apparatus based upon a phenomenon investigated by the staff of the General Electric Company. The apparatus is easy to use, very sensitive, and gives closely repeatable results. As the glass is in contact only with an alloy of platinum, it is possible to work on a sample of glass for months at a time, and perform experiments on the effects of heat treatment of the glass which would be impossible with an apparatus using ordinary refractory materials. In view of the remarks of Mr Paterson, this apparatus would seem to be particularly suitable for his requirements.

In conclusion, I should like again to congratulate the authors for having introduced some measure of co-ordination between the results of previous workers. This is very important.

Prof. W. E. S. TURNER: I should like to express my thanks to Messrs Proctor and Douglas for their work on a subject which has proved to be of great interest and first class importance in the past five or six years. Although their work seems to me to have been excellent, the authors may feel still more assured if I remark that recently I was privileged in America to see two papers by Mr Lillie covering much the same ground as the paper by Messrs Proctor and Douglas and reaching very closely similar conclusions, namely, that the measurements of Washburn and Shelton of the viscosity of different glasses were in themselves made correctly, and that any errors in the final results are to be traced to the calibration factor, and finally that the measurements of English are reasonably well substantiated.

AUTHORS' reply: In reply to Dr English: we agree with him in fixing a viscosity of 1000 c.g.s. units as an approximate lower limit for an apparatus having similar dimensions to our own, owing to frictional errors seriously reducing the accuracy of the measurements at lower viscosities. However, by using a stirrer and pot of

larger diameter this limit could probably be considerably lowered. We should like to thank Dr English for drawing our attention, just prior to the meeting, to a further paper of his which we regret to have overlooked. In this he discusses the differences between his results and those of Mr Stott at the higher temperatures.

In answer to Mr Stott: no visible corrosion of the pot and stirrer could be detected after a test. A new pot and stirrer were used for each glass. As we intended to include lead glasses in the measurements we felt that it was not advisable to use a platinum stirrer and pot, owing to the interaction of lead glass and platinum.

We considered the wire method, but decided in favour of a rotating cylinder apparatus. The wire method is open to two criticisms. Firstly, the calculation of the viscosity from the experimental data involves an accurate knowledge of the surface tension of the glass over the whole range of temperature. Secondly, the glass carried out of the pot by the wire is mainly drawn from the surface layers, and any volatilisation of the glass or incipient surface devitrification would seriously affect the accuracy of viscosity measurements.

## THE BAND SPECTRUM OF LANTHANUM MONOXIDE

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**ABSTRACT.** The spectrum has been observed from  $\lambda$  8700 to  $\lambda$  2850, and the band-heads (most of them not hitherto recorded) arranged into several systems. While the work was in progress Auerbach\* gave high dispersion data for some of the new infra-red heads, and Mecke† briefly reported the analysis of seven systems, having 0, 0 bands at (1)  $\lambda$  4372; (2)  $\lambda$  4418; (3)  $\lambda$  5600; (4)  $\lambda$  7380; (5)  $\lambda$  7404; (6)  $\lambda$  7877; and (7)  $\lambda$  7910. Mecke concluded that (a) systems 3, 5 and 7 have a common final state; (b) so have systems 1 and 2; and (c) the initial states for 1 and 2 appear to be the final states for 4 and 6 respectively.

The author's analysis of 2 differs from Mecke's, the 1, 2 band in the former being the 0, 1 band in the latter. Hence, while Mecke's conclusion (a) is approximately confirmed, (c) becomes untenable if (b) is true, as it probably is. If systems 1 and 2 have states in common with 4 and 6 respectively, they must be the final states in each case. Systems 4 and 6 resemble one another in appearance and in initial and final vibrational frequencies, but probably have no state in common. They may represent the *R* heads of two systems of which 5 and 7 respectively are strong *Q* heads; the pair of systems ( $\Delta\nu_e = 864 \text{ cm.}^{-1}$ ) having a common final state and corresponding to the infra-red  $^2P \rightarrow ^2S$  doublet of Cs ( $\Delta ^2P = 554 \text{ cm.}^{-1}$ ); but there appears to be evidence against this interpretation. Some ultra-violet bands,  $\lambda$  3710 –  $\lambda$  3457, degraded towards shorter wave-lengths, i.e. opposite to those of systems 1...7, have been measured. Eight of these appear to belong to an incompletely traced eighth system due to a transition from the final state of one or more of the above systems, e.g. 3, 5, 7, to the initial state of another, e.g. 1 or 2.

*Appendix.* A brief note is given on the general theory of electronic band spectra of diatomic molecules.

## § 1. INTRODUCTORY

IN the lanthanum section in Volume 5 of Kayser's *Handbuch*‡ are collected data for five groups of bands in the visible region, which have since been assigned to lanthanum oxide§. The bands all degrade towards the red, the most refrangible heads of the groups being at  $\lambda$  4372, 4418, 5380, 5600 and 5863 Å. respectively. The first two groups, for which further data have been given by F. Exner and E. Haschek|| and by J. Ôkubo¶, are similar to one another in intensity and in spacing, and appear on first inspection to be neighbouring sequences of a common band-system; brief examination of the data shows that they are more probably the prominent

\* *Naturwissenschaften*, February 1, 1929.† *Ibid.*‡ *Handbuch der Spectroscopie*, 5, 667 (1910).§ A. Hagenbach and H. Konen, *Atlas of Emission Spectra*, A. S. King's English Edition (1905), p. 30 and charts XIII (strip 127) and XIV (strip 137). Lanthanum sulphate in carbon arc in air.|| *Die Spectren der Elemente bei Normalem Druck*, 2, 117 (1911).¶ *Tôhoku Univ. Sci. Reports*, 11, 95 (1922).

sequences of two closely related band-systems, which will be called systems 1 and 2, for reasons appearing presently. The remaining three groups are easily recognisable as fragments of three neighbouring sequences (with  $n'' - n' = -1, 0$  and  $+1$  respectively) of another band-system, 3.

In the *Tabelle der Bandenspectra*\* Kayser gives approximate wave-lengths for the band-heads in two further lanthanum groups in the red, degrading, like the former bands, in the long-wave direction, and beginning at  $\lambda$  6995 and  $\lambda$  7380 respectively. These groups appear at first sight to be two sequences of one system of double headed bands, but closer investigation shows that in each group alternate bands belong to two separate systems, which will be called 4 and 5.

In October and November 1928 the author photographed and measured a large number of new bands of all the above systems, except system 1, and also two new groups of bands in the near infra-red, somewhat resembling Kayser's red groups and degrading towards longer wave-lengths from  $\lambda$  7877 and  $\lambda$  8453 respectively. Some of these infra-red bands fell naturally into one of the systems already mentioned, namely, system 5; others were arranged in a new system, referred to below as system 7; and the remainder formed fragments of three sequences (one quite definite and two somewhat uncertain) which the author failed to connect either with one another or with the other band-systems. From the conditions of development of the red and infra-red bands it was clear that they belonged to the same spectrum as the earlier known bands in the visible region, and were due to an oxide, which the simplicity of the systems indicates as diatomic, i.e. LaO.

At this stage, when systems 2, 3, 4, 5, and 7 had been recognised and analysed, the investigation had to be put aside for four months on account of pressure of other work. On resumption, some higher dispersion data were obtained for the red and infra-red band-heads, and a description of the work for publication was begun, when the writer's attention was drawn† to two letters which had appeared in the meantime briefly recording an investigation of the same spectrum at Bonn. In the first letter Fr. H. Auerbach‡ gives very precise grating data of most of the band-heads of the two new groups in the infra-red, and in the second Dr R. Mecke§ summarises a vibrational analysis resulting in seven band-systems, the heads of which are given approximately by formulae of the usual type||, namely,

$$\nu_{\text{head}} = (\nu_0 + \kappa) + [a' (n' + \frac{1}{2}) - b' (n' + \frac{1}{2})^2] - [a'' (n'' + \frac{1}{2}) - b'' (n'' + \frac{1}{2})^2],$$

in which the coefficients have the values shown in Table 1. The numbers 1 to 7 adopted throughout the present paper to designate the systems are those used by Mecke.

From a study of the vibrational energy coefficients for the electronic states involved in the seven systems, Mecke concludes that (a) systems 3, 5 and 7 have a

\* *Handbuch der Spectroscopie*, 6, 1036 (1912).

† By Prof. R. S. Mulliken in a letter received April 1.

‡ *Die Naturwissenschaften*, 17, 84 (February 1, 1929).

§ *Ibid.* p. 86.

|| Actually Dr Mecke's formulae were given in the form indicated by the earlier quantum theory, and have here been converted into the new mechanics form.



common final state; (b) systems 1 and 2 have a common final state; (c) the initial state for system 1 appears to be the final for system 4; (d) the initial state for system 2 appears to be the final for system 6. Dr Mecke finally notes that no ultra-violet system has yet been observed which combines one of the systems 3, 5 and 7 with one of the systems 1, 2, 4 and 6.

Table 1. System-origins and vibrational frequency coefficients (Mecke)

System	$(\nu_0 + \kappa), \frac{\text{cm}}{\text{sec}}$ System- origin, $\nu_0$	Initial state		Final state	
		$a'$	$b'$	$a''$	$b''$
1	22874.9	806.3	1.8	826.5	2.0
2*	22638.4	801.8	1.8	826.5	2.0*
3	17886.1	732.85	2.15	816.3	2.20
4	13575.5	750.1	1.96	807.0	1.87
5	13532.0	760.6	2.2	816.6	2.18
6	12719.6	745.5	1.8	801.8	1.8
7	12665.7	762.0	2.2	816.6	2.18

As has already been stated, the author had independently analysed five of these systems, namely, 2, 3, 4, 5 and 7, and had obtained some data for the three sequences which constitute system 6; it is unlikely, however, that he would have succeeded in correlating these sequences without the aid of Dr Mecke's formula for system 6. System 1 was not analysed by the author, as only one sequence had been observed. As a result of the author's observation of a new sequence in system 2 an interpretation different from Dr Mecke's had been arrived at for this system.

While the author's low dispersion data are, of course, far less precise than Fr. Auerbach's excellent grating data in the infra-red, they include several hitherto unrecorded sequences in systems 2, 3, 5 and 7, and also some ultra-violet bands, probably involving some of the electronic energy levels associated with the other systems.

## § 2. THE PRESENT OBSERVATIONS: EXPERIMENTAL DETAILS

The LaO spectrum has been observed as completely as possible from  $\lambda$  8700 to  $\lambda$  2850. The source employed was the long yellow flame which projects from a carbon arc freely supplied with lanthanum nitrate and carrying a current of from 15 to 25 amp. The LaO bands are developed much more intensely in this flame than in the arc itself, which, of course, develops the line spectrum of the La atom predominantly. Four spectrographs have been used in different parts of the spectrum:

(i) a quartz prism Littrow instrument having a dispersion varying from 71 to 12.5 Å./mm. over the range  $\lambda$  8670 to  $\lambda$  4350; this was used in the initial survey of the whole spectrum;

(ii) a glass prism Littrow spectrograph† (Hilger's E 52), with a dispersion of from 48 to 29 Å./mm. over the range for which it was employed in this instance, namely,  $\lambda$  8670 to  $\lambda$  7380;

\* For system 2 the coefficient of  $n'^2$  is given as 3.0 in Dr Mecke's letter, but this is probably a misprint for 2.0, which gives better agreement between the observed and calculated wave numbers.

† In Messrs Adam Hilger's laboratory, at the kind invitation of Mr F. Twyman, F.R.S.

(iii) a glass prism Littrow instrument\* of still higher dispersion, namely, from 26 to 18 Å./mm. over the range,  $\lambda$  8100 to  $\lambda$  7000, for which it was employed;

(iv) a 2.35 m. concave grating spectrograph, giving a dispersion of about 7.3 Å./mm. in the first order, which was used for system 3. For the extreme red and near infra-red bands Kodak kryptocyanine and neo-cyanine plates were used, the iron arc lines being employed as standards of wave-length in these, as in the more refrangible regions.

### § 3. SYSTEM 3: THE GREEN, YELLOW, AND ORANGE BANDS

This system, which it is convenient to describe first, is the most extensive system in the whole spectrum. In the first order of the grating measures have been made of a pair of heads in a large number of bands of six sequences. The bands previously recorded form but small fragments of the — 1, 0 and — 1 sequences, and only in the case of two bands has more than one head been recorded hitherto.

Table 2. System 3; wave-lengths of *R* and *Q* heads

$n', n''$	$\lambda_{\text{air}}$	$n', n''$	$\lambda_{\text{air}}$	$n', n''$	$\lambda_{\text{air}}$	$n', n''$	$\lambda_{\text{air}}$	$n', n''$	$\lambda_{\text{air}}$	$n', n''$	$\lambda_{\text{air}}$
		2, 0	5178.28 80.00	1, 0	5380.37 82.40	0, 0	5599.91 5602.41	0, 1	5866.27 69.37	0, 2	6157.36 61.24
4, 1	5015.39 —	3, 1	5202.73 04.47	2, 1	5405.57 07.59	1, 1	26.00 28.51	1, 2	93.39 96.53	1, 3	85.66 89.57
5, 2	? 39.60 40.92	4, 2	27.31 29.04	3, 2	30.94 32.96	2, 2	52.27 54.66	2, 3	5920.71 23.78	2, 4	6214.07 17.97
6, 3	63.60 64.99	5, 3	52.13 53.78	4, 3	55.50 58.47	3, 3	78.48 80.90	3, 4	48.07 51.16	3, 5	42.62 46.51
7, 4	87.80 89.21	6, 4	77.03 78.78	5, 4	82.16 84.20	4, 4	5705.07* 07.55	4, 5	75.70 78.72	4, 6	71.31 75.17
8, 5	5112.40 †	7, 5	† 5303.81	6, 5	5508.23 10.18	5, 5	31.65 33.96	5, 6	6003.46 06.48	5, 7	6300.08 03.95
9, 6	36.96 38.12	8, 6	27.79 29.17	7, 6	34.13 36.12			6, 7	31.33 34.27	6, 8	29.09 32.93
10, 7	61.56 ? 62.92	9, 7	53.24 54.62	8, 7	60.27 62.21			7, 8	59.31 62.32	7, 9	57.89 62.05
		10, 8	78.81 ? 79.86	9, 8	86.81 ? 88.71			8, 9	87.70 90.56	8, 10	87.49 91.25
								9, 10	6115.93 18.69	9, 11	6417.01 20.67
								10, 11	44.44 47.37	10, 12	46.50 50.05

\* Confused by structure of previous band.

† Hidden by a line.

The wave-lengths are shown in Table 2 and the usual  $n', n''$  arrangement of the wave-numbers of the heads is given in Table 3. Though the visual estimates of the intensities of the bands are not tabulated, it may be stated that they conform to a Condon parabola of maxima; a fact which may be inferred generally from the distribution in Table 3.

\* At the Imperial College, South Kensington, by kind permission of Prof. A. Fowler, F.R.S.



From the fact that the separations in the pairs of heads in Table 3 increase in magnitude with decreasing  $n'$  and with increasing  $n''$ , as well as from the appearance of the heads in the spectrograms, it is concluded that they are the heads of  $R$  and  $Q$  branches respectively. The data are closely represented by the following formulae:

$$\begin{aligned} \nu_{R \text{ head}} &= 17894.1 + [732.6 (n' + \tfrac{1}{2}) - 1.81 (n' + \tfrac{1}{2})^2] \\ &\quad - [815.5 (n'' + \tfrac{1}{2}) - 2.43 (n'' + \tfrac{1}{2})^2] - 0.50 (n' + \tfrac{1}{2}) (n'' + \tfrac{1}{2}); \\ \nu_{Q \text{ head}} &= 17885.8 + [733.2 (n' + \tfrac{1}{2}) - 1.88 (n' + \tfrac{1}{2})^2] \\ &\quad - [816.1 (n'' + \tfrac{1}{2}) - 2.28 (n'' + \tfrac{1}{2})^2] - 0.25 (n' + \tfrac{1}{2}) (n'' + \tfrac{1}{2}). \end{aligned}$$

The small  $(n' + \frac{1}{2})(n'' + \frac{1}{2})$  term is definitely necessary in the case of the  $R$ -head data, and appears also to be required, though less definitely, by the  $Q$ -head data; in the latter case it is difficult to evaluate the coefficient satisfactorily, but it is probably of the order 0.25 as given. This, if sustained by still higher dispersion measures, would imply that the  $Q$  branch is not of the simplest type in which the head is associated with the rotationless state of the molecule.

At the red end of this system the spectrograms show a group of bands degrading in the opposite direction and probably arising from an impurity in the material used. The presence of these bands renders measurement of the heads of the weak sequence + 3 difficult; incomplete data for some bands of this sequence were obtained but are omitted from the tables.

#### § 4. SYSTEMS 4, 5, 6 AND 7: THE EXTREME RED AND NEAR INFRA-RED BANDS

As already mentioned, Kayser has recorded two groups of red bands at  $\lambda$  6995 and  $\lambda$  7380, and Frl. Auerbach and the author have, independently of one another, discovered and measured two near infra-red groups at  $\lambda$  7877 and  $\lambda$  8453. The data for these four groups are collected in Table 4 which also shows the assignment of the bands to Mecke's systems 4, 5, 6 and 7. The writer's data are from plates taken with the two glass Littrow spectrographs. They are more numerous and more precise than those given by Kayser, and also include some bands not recorded by Frl. Auerbach. With the high dispersion used by Frl. Auerbach many strong heads which are apparently single in the author's spectrograms are found to be a close pair with a separation of the same order as that previously measured by Kellner\* and by Ökubo† in the strong blue-violet bands, about 0.5 cm.<sup>-1</sup>.

It will be seen in Table 4 that alternate bands of the  $\lambda$  6995 group belong to two sequences, namely, the - 1 sequences of systems 4 and 5. A given band of the latter system is more intense than the corresponding band of the former.

The  $\lambda$  7379 group is made up of four interlacing sequences, the 0 sequences of systems 4 and 5 accounting mainly for alternate bands at the beginning of the group and the - 1 sequences of systems 6 and 7 for those at the end; the middle of the group where bands of all four systems occur in the order 5, 7, 4, 6 is rather complicated.

In the  $\lambda$  7877 group the most intense bands form the 0 sequence of system 7; these have been measured by both Frl. Auerbach and the author, as also has the

\* *Dissertation* (Bonn, 1904); and Kayser, *Handbuch*, 5, 667 (1910).

† *Loc. cit.*

Table 4. Systems 4, 5, 6 and 7:

Kayser	Author		$n', n''$ and $\delta\nu$		Kayser	Author		$n', n''$ and $\delta\nu$			
	$\lambda_{\text{air}}$	$\nu_{\text{vac}}$	Sys. 4 -1 seq.	Sys. 5 -1 seq.		$\lambda_{\text{air}}$	$\nu_{\text{vac}}$	Sys. 4 0 seq.	Sys. 5 0 seq.	Sys. 6 -1 seq.	Sys. 7 -1 seq.
6995	6994.4	14293.2	1, 0		7380	7379.2	13547.9	0, 0			
7012	7010.9	259.6		1, 0							
7024	24.2	232.6	2, 1	60.4	7404	7402.5	505.2	57.5	0, 0		
7041	40.7	199.2		2, 1							
7055	54.7	171.0	3, 2		7414	10.6	490.4	1, 1	55.9		
7069				60.0							
7071	70.6	139.2		3, 2	7434	33.3	440.3	56.9	1, 1		
7086	85.2	110.0	4, 3	60.4							
7101	7100.9	078.8		4, 3	7444	42.1	433.5	2, 2	56.1		
7117	16.1	048.8	5, 4	60.4							
7132	31.5	018.4		5, 4	7465	64.4	393.2	57.2	2, 2		
7148	47.3	13987.4	6, 5	60.3							
7161	62.3	958.1		6, 5	7485	73.8	376.3	3, 3	55.7		
7179	78.6	926.4	7, 6	60.7							
7194	93.6	897.4		7, 6	7497	95.6	337.5	57.3	3, 3		
	7210.5	864.8	8, 7	60.4							
	25.0	837.0		8, 7	7506.0	319.0		4, 4	56.4		
	42.9	802.8	9, 8	60.8							
	56.9	776.2		9, 8	27.4	281.1		57.9	4, 4		
	75.4	741.2	10, 9	61.1							
	89.2	715.1		10, 9	38.8	261.1		5, 5	56.0		
	7307.8	680.2	11, 10	60.8							
	21.7	654.3		11, 10	59.3	225.1		57.3	5, 5		
	40.9	618.6	12, 11	61.0	62.7	219.2					4, 3
	54.5	593.3		12, 11	71.5	203.8		6, 6	56.3		
	74.7	556.2	13, 12		74.4	198.7				5, 4	59.4
					91.6	168.8		57.3	6, 6		
					96.8	159.8				60.9	5, 4
					7604.5	146.5		7, 7	55.6	6, 5	59.5
					09.5	137.8				60.3	6, 5
					23.8	113.2					
					31.3	100.3					
					44.6	077.5				7, 6	59.3
					57.2	056.0				60.6	7, 6
					*66.0	041.0					
					80.2	016.9				8, 7	59.9
					90.5	000.0					
					7701.4	12981.1				59.2	8, 7
					15.3	957.7				9, 8	60.3
					23.4	944.1					
					37.3	920.8				59.5	9, 8
					50.9	898.2					60.6
					73.8	860.2					
					73.8	860.2				62.3	10, 9
					88.5	835.9				11, 10	

\* Confused by K line  $\lambda$  7664.94 which is strongly developed;  $\lambda$  and  $\nu$  estimated.

o, o band of system 6, which is the first band of this group. There are intervening band-heads, not recorded by Frl. Auerbach, which fall into two sequences. One of these, the + 1 sequence of system 5, consists of quite well defined heads, while the other consists of doubtful heads which were measured with some difficulty but were retained on account of their obviously regular spacing. The latter sequence afterwards proved to be the o sequence of system 6, but it was only with the aid of Mecke's formula (see Table 1) for this system that the author connected these heads with the well-developed o, o band  $\lambda$  7877 at the beginning of the group and with the well-defined - 1 sequence in the latter part of the previous ( $\lambda$  7379) group.

## red and infra-red bands

Frl. Auerbach		Author		$n', n''$ and $\delta\nu$			Frl. Auerbach		Author		$n', n''$ and $\delta\nu$	
$\lambda_{\text{air}}$	$\nu_{\text{vac}}$	$\lambda_{\text{air}}$	$\nu_{\text{vac}}$	Sys. 5 -1 seq.	Sys. 6 0 seq.	Sys. 7 0 seq.	$\lambda_{\text{air}}$	$\nu_{\text{vac}}$	$\lambda_{\text{air}}$	$\nu_{\text{vac}}$	Sys. 6 +1 seq.	Sys. 7 +1 seq.
7876.867 77.22	12691.92 691.34	7876.5	12692.5		0, 0				8408	11890	0, 1	
7910.196 10.34	638.45 638.21	7909.5	639.6			0, 0			8442.5	841.6	1, 2	48.4
7944.61 44.95	583.69 583.14	7943.8	585.0			1, 1	8453.412 53.742	11820.30 825.83	8452.8	827.1		0, 1
7979.35 79.70	528.91 528.36	7973.6	538.0	3, 4		54.6	8489.027 89.996	775.85 775.34	8489.7	775.7		1, 2
		7978.6	530.1			2, 2	8526.216 26.622	725.32 724.76	8526.1	725.5		50.2
		7981.2	526.2	49.7	3, 3				8542.8	702.6		51.0
		8005.3	488.3	4, 5		54.9	8564.025 64.366	673.55 673.09	8563.1	674.5		3, 4
8014.430 14.79	474.07 473.51	8013.6	475.2		58.0		8600.463 00.810	624.09 623.62	8600.6	623.0		50.6
		8018.2	468.2	51.6	4, 4							4, 5
		8038.5	430.7	5, 6		54.7	8638.129 38.400	573.40 572.96	8637.1	574.7		49.2
8049.920 50.26	419.07 418.54	8048.8	420.5		55.3	4, 4			8644.3	565.1		
		8053.9	412.9	51.9	5, 5				8660.4	553.7		
		8072.2	384.8	6, 7		54.9						
8085.75 86.092	364.01 363.52	8084.7	365.6		55.7	5, 5						
		8090.2	357.2	51.8	6, 6							
		8106.1	333.0	7, 8		55.4						
8121.87 22.240	309.06 308.49	8121.1	310.2		56.4	6, 6						
		8127.3	300.8	52.3	7, 7							
		8140.6	280.7	8, 9		54.8						
8158.76 59.105	253.40 252.88	8157.4	255.4		55.7	7, 7						
		8164.3	245.1	53.1	8, 8							
		8176.0	227.6	9, 10		55.2						
8195.60 96.00	198.32 197.72	8194.8	200.2		56.4	8, 8						
		8202.1	188.7	52.2	9, 9							
		8211.0	175.4	10, 11		57.2						
8232.94	143.00					9, 9						

The  $\lambda 8453$  group consists chiefly of a sequence of bands which have been measured by both Frl. Auerbach and the author, namely, the + 1 sequence of the relatively intense system 7. The author's plates show in addition a few fainter heads; two of which fall into the + 1 sequence of the weaker system 6.

The usual  $n', n''$  arrangement of the wave numbers of the heads is shown in Table 5 for systems 4 and 5, in Table 6 for systems 6 and 7; the reason for pairing neighbouring systems in this way will be apparent presently. In each of these four systems a strong 0 sequence is observed with either one or both of the neighbouring sequences - 1 and + 1; this distribution of intensity is characteristic of a relatively

Table 5. Wave-numbers and differences in progressions of systems 5 (upper figures) and 4 (lower figures)

$n''$	0	1	2	3	4	5	6	7	8	9	10	11	12
$n'$	0	1	2	3	4	5	6	7	8	9	10	11	12
0	13505.2 13547.9 744.4												
1	14256.3 13440.3 13400.4 14293.3 802.8 749.9	†											
2	14160.2 13393.2 14232.6 806.0 799.1 746.0		†										
3	14130.2 13375.5 14171.0 801.7 794.7	13397.5 799.5 13376.3 741.3 743.1	12538.0? — — — —										
4	14078.8 13319.0 14110.0 797.7 792.8 737.3 736.8	13376.3 741.3 743.1	12538.0? — — — —	13381.1 792.8 13319.0 — —	12188.3 — — — —								
5	14018.8 13261.1 14048.6 787.7 732.1	13319.0 792.8 13319.0 — —	12538.0? — — — —	13381.1 792.8 13319.0 — —	12188.3 — — — —								
6	13958.1 13203.8 13987.4 780.3 783.6 728.6 728.4	13319.0 792.8 13319.0 — — — —	12538.0? — — — — — —	13381.1 792.8 13319.0 — — — —	12188.3 — — — — — —								
7	13897.4 13168.8 13867.4 780.3 784.2 728.6 728.4	13319.0 792.8 13319.0 — — — —	12538.0? — — — — — —	13381.1 792.8 13319.0 — — — —	12188.3 — — — — — —								
8	13837.0 13113.2 13804.8 781.0 785.2 723.8 723.0	13319.0 792.8 13319.0 — — — —	12538.0? — — — — — —	13381.1 792.8 13319.0 — — — —	12188.3 — — — — — —								
9	13770.2 13000.0 13762.4 776.2 772.4 715.1 716.5	13319.0 792.8 13319.0 — — — —	12538.0? — — — — — —	13381.1 792.8 13319.0 — — — —	12188.3 — — — — — —								
10	13715.1 12944.1 13715.1 771.0 768.7 710.2 710.2	13319.0 792.8 13319.0 — — — —	12538.0? — — — — — —	13381.1 792.8 13319.0 — — — —	12188.3 — — — — — —								
11	13654.8 13680.2												
12	13593.3 13618.2												
13	13556.2												

\* Hidden by 0, 0 band of system 6.

† Hidden by 0, 0 band of system 7.

‡ Hidden by 1, 1 band of system 7.

Table 6. Wave-numbers and differences in progressions of systems 7 (upper figures) and 6 (lower figures)

$n''$	0	1	2	3	4	5	6	7	8	9
0	12639.3 812.5 12692.5 802.5 11827.1 11890									
1		12585.0 809.3 11775.7 11841.6 757.9 754.4								
2			12530.1 804.6 11725.5 749.7							
3				12475.2 800.7 11674.5 746.0						
4					12420.5 796.6 11623.0 741.7					
5						12365.6 790.9 11574.7 735.5				
6							12310.2 12357.2 730.8			
7								12255.4 12300.8 725.7		
8									12200.2 12245.1 720.6	
9										12188.7
10										709.5 1260.2 12898.2

\* Hidden by 0, 0 band of system 7.

† Hidden by 1, 1 band of system 7.

‡ Confused by K line  $\lambda$  7664.04;  $\nu$  estimated.



small change of vibration frequency and of moment of inertia in passing from the initial to the final state of the molecule—a smaller change than that represented by the more open “parabolic” distribution of system 3 (Table 3). This is also seen in the formulae which have been derived from the data, namely:

System

$$4. \nu = 13576.5 + [749.3 (n' + \frac{1}{2}) - 1.93 (n' + \frac{1}{2})^2] - [806.4 (n'' + \frac{1}{2}) - 1.89 (n'' + \frac{1}{2})^2].$$

$$5. \nu = 13532.4 + [759.1 (n' + \frac{1}{2}) - 2.21 (n' + \frac{1}{2})^2] - [814.9 (n'' + \frac{1}{2}) - 2.20 (n'' + \frac{1}{2})^2].$$

$$6. \nu = 12721.1 + [750.2 (n' + \frac{1}{2}) - 2.08 (n' + \frac{1}{2})^2] - [806.6 (n'' + \frac{1}{2}) - 2.13 (n'' + \frac{1}{2})^2].$$

$$7. \nu = 12668.1 + [762.8 (n' + \frac{1}{2}) - 2.29 (n' + \frac{1}{2})^2] - [818.5 (n'' + \frac{1}{2}) - 2.37 (n'' + \frac{1}{2})^2].$$

It is clear from the coefficients that systems 5 and 7 resemble one another, as also do systems 4 and 6. If due allowance be made for the small dispersion used in the infra-red, it will be seen on comparison of the  $[\prime\prime]$  terms in these formulae with those in the formulae already given for system 3, that systems 3, 5 and 7 probably have the same final state; Mecke has independently reached the same conclusion (a), p. 521. This is more definitely indicated by a direct comparison of the vibration frequency differences for these three systems in Tables 3, 5 and 6 than by the coefficients in the formulae.

Systems 4 and 6 are somewhat alike both in their appearance in the spectrograms and in the values of the vibrational frequency differences associated with their initial and final states. Comparison, either by means of the above formulae or by means of the differences in the progressions in Tables 5 and 6, is less conclusive than in the case of systems 5 and 7 on account of the inadequacy of the data for system 6, but it is improbable that 4 and 6 have either a common initial or a common final state.

It is interesting to study these systems from another point of view. In Table 5 it will be seen that the interval between the heads of corresponding bands of systems 4 and 5 increases with decreasing  $n'$  in the  $n'$  progressions and with increasing  $n''$  in the  $n''$  progressions; and Table 6 shows a similar variation of the interval between the heads of corresponding bands of systems 6 and 7. This is exactly the kind of variation which is shown by the interval  $\nu_{R \text{ head}} - \nu_{Q \text{ head}}$  in a system of single bands of the  $PQR$  type, such as system 3 described in the previous section. Hence these observations are in harmony with the interpretation of systems 4 and 5 as a single system, in which 4 represents the  $R$  heads and 5 the  $Q$  heads, and of systems 6 and 7 as a similar system of bands with  $R$  and  $Q$  heads. According to this view, 4, 5 and 6, 7 are a pair of systems forming an electronic doublet with a common final electronic energy level and a pair of initial electronic energy levels having a separation  $\Delta\nu = \nu_6 - \nu_7 = 13532.4 - 12668.1 = 864.3 \text{ cm.}^{-1}$ . For so heavy a molecule as LaO this wide doublet separation is perhaps quite reasonable.

Further, it seems likely that the electronic energy level of the LaO molecule, with 65 extra-nuclear electrons, may be comparable with those of the Cs atom

which contains ten fewer electrons\* and that the pair of systems 7, 6 and 5, 4 may be the LaO counterpart of the Cs doublet  $\lambda\lambda$  8942.46, 8521.12 which is given by transitions from the lowest pair of excited states  $6^2P_{1/2}$ ,  $6^2P_{1/2}$ , to the normal state  $6^2S_{1/2}$  of the Cs atom. This would imply that the band-systems are due to transitions  $^2\Pi \rightarrow ^2\Sigma$ , the common final  $^2\Sigma$  state being the normal state of the molecule, and the initial  $^2\Pi$  states the lowest two excited states; the doublet separation in Cs,  $^2P_{1/2} - ^2P_{3/2} = 11732.3 - 11178.3 = 554 \text{ cm.}^{-1}$ , and in LaO  $^2\Pi_{1/2} - ^2\Pi_{3/2} = 864 \text{ cm.}^{-1}$ , which is not unreasonable.

We must now see whether the intervals 4-5 and 6-7, which are about 44 and  $53 \text{ cm.}^{-1}$  respectively, are of the order of magnitude to be expected for  $\nu_{R \text{ head}} - \nu_{Q \text{ head}}$  when compared with system 3 in which this interval is about  $8 \text{ cm.}^{-1}$ . Now the interval  $\nu_{R \text{ head}} - \nu_{Q \text{ head}} = h/8\pi^2c(I_0' - I_0'')$  in the o, o band; i.e. it is inversely proportional to the change in the moment of inertia of the molecule in the initial and final states. But  $(I_0' - I_0'')$  increases and decreases in magnitude with  $(\omega_0'' - \omega_0')$ , the change in the vibrational frequency, which in systems 4, 5, 6 and 7 is only about two-thirds of the value in system 3, as may be seen from the foregoing formulae. Hence we should expect  $\nu_{R \text{ head}} - \nu_{Q \text{ head}}$  to be larger in the systems 4, 5 and 6, 7 than in system 3, though not perhaps so much as  $44/8$  or  $53/8$  times. Here, then, appears to be evidence against the coupling of the systems, the intervals 4-5 and 6-7 being apparently too large.

\* Mr R. W. B. Pearse has suggested to the author that the basis of this comparison may be that in oxides, fluorides, etc. (but not hydrides) of heavy metallic atoms each constituent atom of the molecule not only retains its own two K electrons, but also has a complete group of eight L electrons independently of the presence of the other constituent atom, and that the remaining electrons constitute an outer structure of the whole molecule similar to that of the atom with ten fewer electrons. Thus we have the following comparable atomic and molecular electron configurations:

Atoms	K	L	M	N	O	P	Molecules	K, K	L, L	Outer
K, Ca <sup>+</sup> (19)	2	8	8	1	—	—	ScO, CaF (29)	2, 2	8, 8	8 1 —
Rb, Sr <sup>+</sup> (37)	2	8	18	8	1	—	YO, SrF (47)	2, 2	8, 8	18 8 1 —
Cs, Ba <sup>+</sup> (55)	2	8	18	18	8	1	LaO, BaF (65)	2, 2	8, 8	18 18 8 1
Ca (20)	2	8	8	2	—	—	TiO (30)	2, 2	8, 8	8 2 —
Sr (38)	2	8	18	8	2	—	ZrO (48)	2, 2	8, 8	18 8 2 —
Ba (56)	2	8	18	18	8	2	HfO (66)	2, 2	8, 8	18 18 8 2

From this point of view Miss F. Lowater, *Nature*, 123, 644 (1929), has recently examined the band systems of TiO, and the writer is investigating those of ScO and YO. R. C. Johnson's comparison of the energy levels of CaF, SrF and BaF with those of Ca<sup>+</sup>, Sr<sup>+</sup> and Ba<sup>+</sup> (*Proc. Roy. Soc. A*, 122, 161, 189 (1929)) is of a similar nature, though the electron structures suggested by Johnson differ from those adumbrated by Pearse. In 1925 Mulliken, *Phys. Rev.* 26, 562 (1925), compared some light diatomic molecules with the atom containing ten less electrons; e.g. BeF, BO, CN, CO<sup>+</sup>, N<sub>2</sub><sup>+</sup> (13 electrons) with Li, and MgF, AlO, SiN (21 electrons) with Na, but they have usually been compared, by Mulliken and others, with the atom having two fewer electrons, the constituent atoms of the molecule being supposed to retain only their K electrons; thus:

Atoms	K	L	M	N	Molecules	K, K	Outer
Na (11)	2	8	1	—	BO, BeF (13)	2, 2	8 1 —
K (19)	2	8	8	1	AlO, MgF (21)	2, 2	8 8 1
Mg (12)	2	8	2	—	CO, N <sub>2</sub> (14)	2, 2	8 2 —
Ca (20)	2	8	8	2	SiO, CS (22)	2, 2	8 8 2

## § 5. SYSTEMS 1 AND 2; THE BLUE-VIOLET BANDS

The bands in the blue-violet region occur in five short ranges and are accordingly shown in five divisions of Table 7:

(a) An apparently continuous range, beginning with a fairly well defined edge at  $\lambda 4348.2$  and extending with gradually increasing intensity to  $\lambda 4371.9$ . The quartz Littrow spectrograph reveals no definite division into a sequence of bands but there appear to be two vague heads at about 21 and 43  $\text{cm}^{-1}$  respectively from the edge.

(b) The sequence of very strong bands beginning at  $\lambda 4371.9$  and occurring at intervals of about 20  $\text{cm}^{-1}$ . The heads of these bands have been measured under high dispersion by Kellner and by Okubo and found to be very close doublets with a separation of about 0.5  $\text{cm}^{-1}$ , which has also been found in system 7 by Frl. Auerbach. This is the 0 sequence of Mecke's system 1.

(c) A similar and equally strong sequence of bands beginning at  $\lambda 4418.2$  and occurring at rather greater intervals, about 25  $\text{cm}^{-1}$ ; the doublet separation as measured by both Kellner and Okubo is again about 0.5  $\text{cm}^{-1}$ . This is the 0 sequence of Mecke's system 2.

(d) Some faint bands running on from the end of (c) to about  $\lambda 4500$ , and followed by a range of apparently continuous spectrum between about  $\lambda 4535$  and about  $\lambda 4560$ , in which no band-heads can be measured on the quartz spectrograms.

(e) A sequence of regularly spaced bands similar to, but very much weaker than, (b) and (c), beginning at  $\lambda 4580.8$  and occurring at intervals of about 20  $\text{cm}^{-1}$ . They have been measured on plates taken with the quartz spectrograph (dispersion here about 15  $\text{\AA./mm.}$ ). Though the heads appear to be single, it is probable that under adequate dispersion they would be found to be double, like (b) and (c), with a separation of about 0.5  $\text{cm}^{-1}$ .

Spectrograms in which (a), (d) and (e) are measurable show (b) and (c) very much over-exposed. For the two latter Okubo's [I.A.] data, which are more complete than Kellner's [R.A.] data, are included in Table 7 with the writer's observations of (a), (d) and (e).

*System 2.* According to Mecke's formula for system 2, the coefficients of which have been given in Table 1, the 0 sequence is (c) as would be expected, and the +1 sequence is (e) with the first band  $\lambda 4580.8$  omitted. There is, in fact, no place in Mecke's system 2 for this band, although in the writer's plates it clearly belongs to the same sequence as the rest in (e) and is just as genuine a band as the next band  $\lambda 4585.0$  which is the 0, 1 band in Mecke's system. According to the writer's assignment of  $n'$ ,  $n''$  values, which is shown in Tables 7 and 8,  $\lambda 4580.8$  is the 0, 1 band, and the system is approximately represented by the formula

$$\nu = 22639.5 + [782.7 (n' + \frac{1}{2}) - 2.39 (n' + \frac{1}{2})^2] - [807.3 (n'' + \frac{1}{2}) - 2.27 (n'' + \frac{1}{2})^2].$$

This expression shows at once that the change in vibration frequency ( $\omega'' - \omega'$ ), and therefore in moment of inertia ( $I' - I''$ ) for this system, is even smaller than the changes in systems 4, 5, 6 and 7; the intensity distribution is in full accordance

Table 7. Systems d 2 and other ue-violet bands

(b)

$\lambda_{\text{air}}$ (Author)	$\nu_{\text{vac.}}$ and $\delta\nu$	$\lambda_{\text{air}}$ (Okubo)	$\nu_{\text{vac.}}$ and $\delta\nu$	$n', n''$ Sys. 1	$\lambda_{\text{air}}$ (Okubo)	$\nu_{\text{vac.}}$ and $\delta\nu$	$n', n''$ Sys. 2	$\lambda_{\text{air}}$ (Author)	$\nu_{\text{vac.}}$	$\lambda_{\text{air}}$ (Author)	$\nu_{\text{vac.}}$ and $\delta\nu$	$n', n''$ Sys. 2
4348.2	22901.6 21.1	4371.869 -874	22867.11 66.56 20.14	0, 0	4418.170 -265	22627.47 26.90 25.25	0, 0	4468.7? 71.1	22371.6 350.8	4580.78	21824.2 20.0	0, 1
52.2	970.5 21.7		20.12			25.19		73.0? 79.6	350.1 317.2	85.00	804.2 20.9	1, 2
56.3	948.8 21.1	75.722 -824	46.97 46.44 20.54	1, 1	23.106 -188	02.23 01.80 25.16	1, 1	81.0? 83.6? 85.8	310.2 297.3 286.3	89.39	783.3 20.3	2, 3
These are faint heads (?) in apparently continuous spectrum from the edge at $\lambda$ 4348.2 to the very strong head $\lambda$ 4371.9 (0, 0 of system 1)												
		79.660 -762	26.43 25.90 20.08	2, 2	28.036 -136	22577.06 76.55 25.33	2, 2	89.1 and unresolved spec- trum from about $\lambda$ 4535 to about $\lambda$ 4560	270.0 258.5	98.14	741.9 21.1	4, 5
		83.517 -567	06.35 06.09 20.61	3, 3	33.008 -060	51.73 51.47 25.08	3, 3			07.26	698.8 22.4	6, 7
		87.482 -603	22785.74 85.11 20.98	4, 4	37.942 38.060	26.66 26.07 25.40	4, 4			11.82	677.4 21.4	7, 8
		91.644 -741	64.14 63.64 21.60	5, 5	43.070 -165	00.67 00.18 25.99	5, 5			16.85	653.7 23.7	8, 9
		95.655 -742	43.37 42.92 20.72	6, 6	48.190 -203	22474.77 74.25 25.93	6, 6			22.58	636.9 26.8	9, 10
		4400.045 -125	20.68 20.27 22.69	7, 7	53.381 -431	48.52 48.06 26.25	7, 7					
		04.741 -833	24.22 24.29 22.65	8, 8	58.684 —	21.87 — 26.65	8, 8					
			22696.46 95.98			— ? 23.55						
					764.368 —	22393.32 —	9, 9					
					For 9, 9 the writer's measure is							
					4463.98	22395.3 26.6						

Table 8. Wave-numbers and differences in progressions of system 2

$n''$	0	1	2	3	4	5	6	7	8	9	10
0	22627.5803.3	21824.2									
1		22778.0									
2		22602.2	21801.2								
3			772.8	21783.3							
4				798.4	21763.0						
5				22551.7	788.7	21741.9					
6					753.6	21721.2					
7					22526.6	784.7	21700.7	21698.8			
8						758.8	22171.8	749.7	21677.4		
9							22148.5	771.1	22431.5	21653.7	
									744.5	739.6	
									22363.3	766.4	21026.9

with so small a change, the 0 sequence being very much more intense than the + 1 sequence, and the - 1 sequence being not even detected (the 1, 0 band should be at  $\lambda$  4271.4).

From Mecke's analysis it appears that the initial state for system 2 is the same as the final state for system 6: see conclusion (d) on p. 522. The interpretation here suggested, however, conflicts with this conclusion, and appears to show rather that if systems 2 and 6 have a state in common it is the final state of both. This may be seen either by comparing the [''] term in the above formula and the system 6 formula given on p. 530, or by comparing the vibration frequency differences in the  $n''$  progressions of the systems in Tables 6 and 8, due allowance being made for the fact that the observations of system 6 are less satisfactory than those of the other systems.

*System 1.* Mecke's expression for this system (see p. 522) is based on the interpretation of (b) of Table 7 as the 0 sequence, and indicates that the + 1 sequence should begin at  $\lambda$  4535.5 (0, 1), where the writer's plates show the unresolved range (d), and that the - 1 sequence should begin at  $\lambda$  4224, where no bands can be detected in these plates. If we accept Mecke's analysis for system 1 and the present interpretation of system 2, the common state for these two systems can only be the initial of system 1 and the final of system 2, rather than the final of each as concluded by Mecke, see (b), p. 522. This, however, seems less probable than either of the following alternatives.

First, we may assume as correct Mecke's conclusion that systems 1 and 2 have a common final state, but suppose it to have vibrational energy levels given by the [''] term now found for system 2 instead of the term given by Mecke, namely  $826.5(n'' + \frac{1}{2}) - 2.0(n'' + \frac{1}{2})^2$ . We then derive for the observed sequence of system 1 the formula

$$v = 22876.8 + [788.2(n' + \frac{1}{2}) - 2.52(n' + \frac{1}{2})^2] - [807.3(n'' + \frac{1}{2}) - 2.27(n'' + \frac{1}{2})^2],$$

which shows that the initial state is different for any state involved in the other systems, and so conflicts with Mecke's suggestion (c), p. 522, that the initial state of system 1 is the final state of system 4.

Alternatively we may assume, until prohibited by the discovery of an additional sequence of system 1, that systems 1 and 2 have a common initial state, with vibrational energy levels given by the [''] term now found for system 2. The observed sequence of system 1 is then represented by

$$v = 22876.8 + [782.7(n' + \frac{1}{2}) - 2.39(n' + \frac{1}{2})^2] - [801.8(n'' + \frac{1}{2}) - 2.14(n'' + \frac{1}{2})^2],$$

which shows that the final state is not one of those involved in any other system.

These systems have several unusual features: e.g. a gradual increase, instead of decrease, of the interval between consecutive bands in each sequence with increasing  $n'$ ,  $n''$ . It may be noted also that, according to Ôkubo's measurements, the 3, 3 band of each system has an interval between its heads about half as large as that in most of the bands; for each of these two bands Kellner measured only the second head.

## § 6. ULTRA-VIOLET BANDS

Band structure extends, with very little interruption, from about  $\lambda$  3800 to  $\lambda$  3450 with great complexity in several parts of the range. All the bands whose heads are measurable degrade towards the further ultra-violet, i.e. in the opposite direction to those of the systems already described. They form fragments of several sequences, which clearly belong to more than one band-system. Details of observations made with the quartz Littrow spectrograph are shown in Table 9; in this region the dispersion of the instrument becomes usefully large, being on an average about equal to that of the first order of the 2.35 m. grating.

Table 9. Heads of ultra-violet bands (degraded towards the further ultra-violet)

Intensity	$\lambda$ air	$\nu$ vac. and $\delta\nu$	Notes	Intensity	$\lambda$ air	$\nu$ vac. and $\delta\nu$	Notes
3	3709.64	26949.2	*†	5	3500.18	28033.2	
				5?	65.01	035.4	
1	3672.32	27223.0		4	60.95	074.4	<sup>39.0</sup>
2	68.44	267.7	<sup>43.7</sup>	3	58.35	110.7	<sup>36.3</sup>
2	60.94	307.6	<sup>39.9</sup>	2	52.05	144.7	<sup>34.0</sup>
2?	56.08	343.9	<sup>36.3</sup>	1	09.57	485.4	
6	14.86	655.7	*	2?	09.28	487.8	§
6?	14.49	658.6	†	1	05.60	517.7	
6	11.50	681.5	§	1	3457.11	917.7	
6	08.09	707.6	<sup>25.8</sup>				
6	04.57	734.7	<sup>26.1</sup>				
			<sup>27.1</sup>				

\* Head confused with a line.

† This is the strongest of several bands, the heads of which cannot be located definitely.

‡ Heavier band structure occurs in the ranges  $\lambda$  3850– $\lambda$  3630 and  $\lambda$  3625– $\lambda$  3616, but no heads are measurable.

§ Possibly a line.

|| The band structure from these four strong heads extends to about  $\lambda$  3575. There is not a trace of the CN heads,  $\lambda\lambda$  3590.4, 3585.9, 3583.9.

Though no complete system can be traced, it may be noted briefly that eight of the observed bands appear to belong to two sequences of one system, as shown in Table 10.

Table 10. Part of ultra-violet system

			$\pi'$
27223.0			
810.2			
28033.2 765.5	27257.7		
	806.7		
	28074.4 766.8	27307.6	
		803.1	
		28110.7 766.8	27343.9
			800.8
			28144.7
$\pi'$			

The probable significance of this lies in the fact that it exhibits vibrational frequency differences of the same orders of magnitude as those in some of the

systems already described, but with the larger differences now in the  $n'$  progressions instead of the  $n''$  progressions as in the former systems; this, of course, should be the case in a system of bands degraded towards the ultra-violet. The system suggested by these bands would appear to have as initial state the final state of one or more of the other systems, e.g. 3, 5 and 7, and as final state the initial state of system 1 or 2. Exactly which systems are involved in this combination is uncertain because  $n'$ ,  $n''$  assignments are not possible at present. If systems 5 and 7 are, in fact, involved they cannot represent the electronic doublet corresponding to the infra-red  $^2P \rightarrow ^2S$  doublet of Cs as discussed on p. 531, their final state being an excited, and not the normal, state.

### § 7. SUMMARY OF CONCLUSIONS

The results of the analysis described in the foregoing sections are collected in Table 11, which shows the coefficients in the formulae which have been obtained from the present observations for the band-heads of the seven systems. By means

Table 11. System origins and vibrational frequency coefficients. (Author)

System	$(\nu_e + \kappa)$	Initial state		Final state	
		$a'$	$b'$	$a''$	$b''$
1	22876.8	} Either Or	788.2	807.3	2.27
2	22639.5		782.7	801.8	2.14
3	17894.1	} R Q	782.7	807.3	2.27
4	17885.8		732.6	815.5	2.43
5	13576.5		733.2	816.1	2.28*
6	13532.4		749.3	806.4	1.89
7	12721.1		759.1	814.9	2.20
	12688.1		750.2	806.6	2.13
			762.8	818.5	2.37

\* These coefficients for system 3 apply only if the small terms in  $(n' + \frac{1}{2})(n'' + \frac{1}{2})$ , given on p. 525, but omitted here, are included.

of this and Table 1 we may readily compare the present results with Mecke's. The initial vibration frequencies, and also the final vibration frequencies, are of so nearly the same order of magnitude that the identification of a given electronic state in different systems is at present a matter of some uncertainty; for this purpose it is better to compare the observed frequency differences in the progressions of the systems than to compare the coefficients in their formulae. The following deductions are made:

(i) Mecke's conclusion (a), p. 521, that systems 3, 5 and 7 have a common final state is approximately confirmed by the present observations. (It may be noted that Mecke's formulae for systems 5 and 7 are apparently derived with the same  $['']$  term for each, while the author's are obtained quite independently of one another from the data for the individual systems.)

(ii) The chief differences between the results arise from the fact that system 2 is differently interpreted. The author's interpretation of system 2 does not neces-



sarily imply that Mecke's conclusion (b), p. 522, that systems 1 and 2 have a common final state, needs revision. These two systems have one state in common, but with the data yet available it may be either the initial or the final state of each.

(iii) Mecke's suggestion (c), p. 522, that the initial state for system 1 may be the final for system 4 is no longer tenable if (ii) is accepted; if these two systems have a state in common it can only be the final of each.

(iv) Similarly, while Mecke suggests, (d), p. 522, that the initial state for system 2 may be the final for system 6, the present analysis shows that these two systems probably have a common final state.

(v) Systems 4 and 6 are very much alike, but from the data at present available for the latter it is improbable that they have a common initial or a common final state. It may be that 4 and 5 form one system of *R* and *Q* heads and that 6 and 7 form another similar system, the pair having a common final state and initial states differing by  $864 \text{ cm.}^{-1}$ , and possibly corresponding to the Cs strong infra-red doublet  $^2P \rightarrow ^2S$  in which  $\Delta^2P$  is  $554 \text{ cm.}^{-1}$ . There are, however, arguments against this view.

(vi) Some ultra-violet bands degraded in the opposite direction to those of systems 1-7 have been observed; although no complete system can be traced it is probable that some of the bands belong to an eighth system which is due to transition from the final state of one or more of the above systems, e.g. 3, 5, 7, to the initial state of another, e.g. 1 or 2.

#### § 8. ACKNOWLEDGMENTS

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### APPENDIX

#### A NOTE ON THE ELECTRONIC BAND SPECTRA OF DIATOMIC MOLECULES

As no account of the analysis of a band spectrum has hitherto been read before the Physical Society, the writer has been asked to add, as an appendix, an explanatory general note.

Theory and experiment agree in attributing line spectra to atoms and band spectra to molecules. The spectra of diatomic molecules, with which we are at present concerned, are of the type which used to be aptly described as "fluted spectra." Examined under low dispersion, each *band* or "fluting" has a sharp edge or *head* from which the intensity falls off in the direction of either increasing wave-number\* (in which case the band is said to *degrade* towards the ultra-violet) or decreasing wave-number (band degraded towards the infra-red). In many spectra

\* Number of waves in 1 cm. *in vacuo* =  $\nu_{\text{vac}} = 10^8/(\lambda_{\text{vac}} \text{ in } \text{\AA.}) \text{ cm.}^{-1}$ .

it is easy to recognise a *sequence* of neighbouring bands distributed with obvious regularity over a limited range; and a number of such sequences constitute a *band-system*. The entire *spectrum* of one molecule consists of a number of systems.

Thus the well-known *band* of CN with a *head* near  $\lambda$  3883 is the first of a *sequence* in which the succeeding band-heads are near  $\lambda$  3871, 3862, 3854. This sequence and three others, whose first (longest-wave) band-heads are near  $\lambda$  4606,  $\lambda$  4216 and  $\lambda$  3590 respectively, constitute the so-called "violet" *system* of CN, in which all\* the bands degrade to the ultra-violet. In the CN *spectrum* there is one other known system, the "red" system, in which all the bands degrade towards the infra-red.

With sufficiently high resolving power a single band is seen to consist of a very large number of closely spaced band-*lines*, which were recognised by early investigators as belonging to two or more series in which the spacing is immeasurably small at the head, and increases at first rapidly and afterwards more slowly with increasing distance from the head, the intensities of the lines at the same time diminishing. The strongest lines are not in general those at the head, the high intensity of the head being due to close packing rather than to high individual intensities of the lines. This early division of a band into series has given place to the present division into *branches*, the word *series* now being reserved for an entirely different purpose, namely, to designate a succession of systems which are found in a few molecular spectra (notably  $H_2$  and  $He_2$ ) to follow the Rydberg-Ritz distribution which is more often found in atomic line spectra.

In molecular, as in atomic, spectra the theory attributes the emission of a line of wave-number  $\nu$  cm.<sup>-1</sup> (frequency  $\nu c$  sec.<sup>-1</sup>) to a transition in the emitter from an excited state (or energy level) in which the energy is  $E'$  to a less excited, or the unexcited, state, of energy  $E''$ , in accordance with the quantum condition  $h\nu c = E' - E''$ . The absorption of the same line accompanies the opposite transition  $E'' \rightarrow E'$ . Whereas the total energy  $E$  of an atom in a given state is regarded as almost entirely electronic,  $E_e$ , that of a molecule is regarded somewhat arbitrarily as the sum of several parts, the chief of which are electronic energy ( $E_e$ ), energy of nuclear vibration ( $E_n$ ), and energy of molecular rotation ( $E_m$ ), where  $E_e > E_n > E_m$ . In other words, a molecule has a number of fairly widely spaced *electronic* energy levels (specified by a group of electronic quantum numbers collectively denoted by  $e$ ); each electronic level has associated with it a set of more closely spaced *vibrational* energy levels (specified by successive values of a vibrational quantum number  $n$ ), and each of these has a set of much more closely spaced *rotational* energy levels (specified by successive values of a rotational quantum number  $j$ , of which  $m$  is the component† measuring the nuclear angular momentum in units  $h/2\pi$ ). Thus the wave-number

\* Excepting, for sake of strict accuracy, certain bands known as the "tail bands."

† The other components of  $j$ , which measure the electronic angular momentum in units  $h/2\pi$ , will not be considered in this note. Formerly  $m$  was regarded as the true quantum number, but now it is the *total* and not the *nuclear* angular momentum that is quantised, and  $j$  takes integral or half-integral values increasing by unity, while generally  $m$  does not.

of the line emitted in a transition  $E' \rightarrow E''$ , the ' and '' denoting the more excited and the less excited states respectively, is

$$\begin{aligned}\nu &= \{(E_e' + E_n' + E_m') - (E_e'' + E_n'' + E_m'')\}/hc \\ &= (E_e' - E_e'')/hc + (E_n' - E_n'')/hc + (E_m' - E_m'')/hc \\ &= \nu_e + \nu_n + \nu_m \quad \dots\dots(1),\end{aligned}$$

where  $\nu_e$ ,  $\nu_n$  and  $\nu_m$  are regarded as three parts of the whole  $\nu$ , and  $\nu_e > \nu_n > \nu_m$  in the general case when  $E_e$ ,  $E_n$  and  $E_m$  all change. For a given band  $\nu_m$  varies from line to line, while  $\nu_e + \nu_n$  is constant and defines the *band-origin* ( $\nu_m = 0$ ). For a given system  $\nu_n$  varies from band to band,  $\nu_e$  being constant and defining the *system-origin* ( $\nu_n = 0$ ,  $\nu_m = 0$ ).

A system for which both  $\nu_e = 0$  and  $\nu_n = 0$  consists of a single band known as a *rotation* band;  $\nu_m$  is so small that such bands are found only in the far infra-red. A system for which  $\nu_e = 0$  but  $\nu_n \neq 0$  is known as a *vibration-rotation* band-system;  $\nu_n$  is so much greater than  $\nu_m$  that such bands lie in the nearer infra-red. A system for which  $\nu_e \neq 0$  is known as an *electronic* band-system;  $\nu_e$  is such that these systems occur anywhere from the near infra-red to the Lyman region. In this note we must briefly consider only the third type.

The energy of an harmonic vibration of the molecule is given by

$$E_n = hc \omega_0 \{(n + \frac{1}{2}) - x(n + \frac{1}{2})^2\}, \quad n = 0, 1, 2, 3, \dots \quad \dots\dots(2),$$

according to the new quantum mechanics\*,  $c\omega_0 \text{ sec.}^{-1}$  (or  $\omega_0 \text{ cm.}^{-1}$ ) being the frequency of vibration of infinitesimal amplitude for the non-rotating molecule, and  $x$  a small constant ( $x = 0$  for simple harmonic vibration). The electronic transition involves changes in both  $\omega_0$  and  $x$ , and for the *band-origins* in the system arising from the transition we have\*

$$\begin{aligned}\nu_0 &= \nu_e + (E_n' - E_n'')/hc \quad \dots\dots(3). \\ &= \nu_e + [\omega_0' (n' + \frac{1}{2}) - \omega_0' x' (n' + \frac{1}{2})^2] - [\omega_0'' (n'' + \frac{1}{2}) - \omega_0'' x'' (n'' + \frac{1}{2})^2]\end{aligned}$$

Since  $\nu_e$  (or  $E_e' - E_e''$ ) is positive and large compared with  $\nu_n$  (or  $E_n' - E_n''$ ), the latter may be positive, zero, or negative, and the values of  $n'' - n'$  for the bands may accordingly be of either sign (not restricted to  $\pm 1$ ) or zero.

As the positions of the *origins* are known for comparatively few bands, we must consider the positions of the band-heads, by discussing briefly the line structure of a simple type of electronic band. The energy of rotation of a molecule may be written as  $E_m = hc.F(j)$ , where  $F(j)$  is a function which differs in form from one electronic state of the molecule to another. Its simplest forms are  $Bj(j+1)$  and  $B(j+\frac{1}{2})^2$  where  $B = h/8\pi^2cI = 27 \times 10^{-40}/I$ ,  $I$  being the moment of inertia of the molecule. Much more complicated forms of  $F(j)$  are frequently necessary.

\* The older quantum theory gave:

$$E_n = hc\omega_0 (n - xn^2), \quad n = 0, 1, 2, 3, \dots \quad \dots\dots(2_0),$$

$$\nu_0 = \nu_e + [\omega_0' n' - \omega_0' x' n'^2] - [\omega_0'' n'' - \omega_0'' x'' n''^2] \quad \dots\dots(3_0).$$

In every case where it has been possible to apply an adequate test, the new mechanics has been found to represent the observational data more accurately. It is therefore reasonable to extend its use to cases where no test is possible and the older theory might serve equally well.

For our present purpose it will suffice to use the approximate form  $F(j) \doteq Bm^2$  first given in the older quantum theory.

The electronic transition  $E_e' \rightarrow E_e''$  is accompanied by a change in  $I$  as well as of  $\omega_0$ ,  $\alpha$  and other molecular constants. Hence the wave number of the  $m' \rightarrow m''$  line of the  $n' \rightarrow n''$  band is given by

$$\begin{aligned}\nu &= \nu_e + \nu_n + (E_{m'}' - E_{m''})/hc \\ &= \nu_e + \nu_n + F'(j') - F''(j'') \doteq \nu_e + \nu_n + B'm'^2 - B''m''^2 \quad \dots\dots(4).\end{aligned}$$

The change  $j'' - j'$  is restricted to  $-1$ ,  $0$ , and  $+1$ , and the lines corresponding to each of these three values constitute a *branch* of the band, the branches being called the *R* or "positive," the *Q* or "zero" and the *P* or "negative" respectively. Putting  $(m'' + 1)$ ,  $m''$  and  $(m'' - 1)$  in turn for  $m'$  in (4)\*, we obtain rough expressions for the branches, namely,

$$\begin{aligned}\nu_R &\doteq \nu_e + \nu_n + B' + 2B'm'' + (B' - B'')m''^2 \\ \nu_Q &\doteq \nu_e + \nu_n \quad \quad \quad + (B' - B'')m''^2 \\ \nu_P &\doteq \nu_e + \nu_n + B' - 2B'm'' + (B' - B'')m''^2 \quad \dots\dots(5).\end{aligned}$$

If  $m''$  is plotted against  $\nu_R$ ,  $\nu_Q$ , and  $\nu_P$ , i.e. in a Fortrat diagram, a parabola is obtained in each case with its axis parallel to the  $\nu$  axis, the vertices being given by

$$\begin{aligned}m''_{R \text{ head}} &\doteq B'/(B'' - B'); \quad \nu_{R \text{ head}} \doteq \nu_e + \nu_n + B'B''/(B'' - B') \\ m''_{Q \text{ head}} &\doteq 0 \quad \quad \quad ; \quad \nu_{Q \text{ head}} \doteq \nu_e + \nu_n \\ m''_{P \text{ head}} &\doteq B'/(B' - B''); \quad \nu_{P \text{ head}} \doteq \nu_e + \nu_n - B'B''/(B' - B'') \quad \dots\dots(6).\end{aligned}$$

Now if there is a decrease in  $I$  during the emission, i.e.  $I' > I''$  and  $B' < B''$ ,  $m''_{R \text{ head}}$  is positive and  $m''_{P \text{ head}}$  negative; thus the successive *R* lines of increasing  $m''$  become closer together as they recede from the band-origin ( $\nu_0 = \nu_e + \nu_n$ ) towards higher  $\nu$ , form a head at about  $B'B''/(B'' - B')$  cm.<sup>-1</sup> above  $\nu_0$ , and then gradually become wider apart with diminishing  $\nu$  and still increasing  $m''$ ; the *P* lines of increasing  $m''$  do not form a head, but slowly become wider apart as they recede from  $\nu_0$  in the direction of lower  $\nu$ ; the *Q* branch, which is present in the bands of some, but not all, systems, starts with a head very near to  $\nu_0$  and runs away from the *R* head. Such a band degrades from its *R* and *Q* heads towards the infra-red.

If, on the other hand, there is an increase in  $I$  during the emission, i.e.  $I' < I''$  and  $B' > B''$ ,  $m''_{P \text{ head}}$  is positive and  $m''_{R \text{ head}}$  negative; the *P* lines now form a head at about  $B'B''/(B' - B'')$  cm.<sup>-1</sup> below  $\nu_0$ , the *R* lines now widen out without forming a head, and the *Q* lines again start with a head near  $\nu_0$  but now run away from the *P* head. Such a band degrades from *P* and *Q* heads towards the ultra-violet.

We must omit discussions of the intensities of the lines in the branches, the missing lines near the origin, perturbations, the application of the combination principle, and the types of doublets and triplets arising from certain physical causes; important as these all are for the rotational quantum analysis of the bands

\* Strictly this should not be done, since generally  $m$  does not change by integral values as  $j$  does.

and for the recognition of the types and multiplicities of the initial and final electronic levels.

For each electronic state of the molecule the moment of inertia increases with the vibrational energy in a way expressed by

$$B'_{n'} = B'_0 - \alpha' (n' + \frac{1}{2}); \quad B''_{n''} = B''_0 - \alpha'' (n'' + \frac{1}{2}) \dots \dots (7),$$

where  $\alpha'$  and  $\alpha''$  are positive constants for the upper and lower electronic states. (For the sake of brevity the suffixes  $n'$  and  $n''$  have been omitted from  $I'$ ,  $B'$  and  $I''$ ,  $B''$  in the above discussion). Hence the interval  $B'_{n'} B''_{n''} / (B''_{n''} - B'_{n'})$  between the  $R$  or  $P$  head and the band-origin or the  $Q$  head varies from band to band throughout the system, and, while formula (3) for the band-origins approximately represents the  $Q$  heads, it must be modified in order to represent the  $R$  and  $P$  heads, thus

$$\begin{aligned} \nu_{\text{head}} = (\nu_e + \kappa) + [a' (n' + \frac{1}{2}) - b' (n' + \frac{1}{2})^2] \\ - [a'' (n'' + \frac{1}{2}) - b'' (n'' + \frac{1}{2})^2] + \theta (n' + \frac{1}{2}) (n'' + \frac{1}{2}) \dots (8). \end{aligned}$$

The constant  $\kappa$  is positive for  $R$  and negative for  $P$  heads, and the coefficients  $a'$ ,  $b'$ ,  $a''$ ,  $b''$  differ appreciably from the corresponding coefficients in (3). Low dispersion data for band-heads do not often permit of the evaluation of the coefficient  $\theta$ , in which case the  $(n' + \frac{1}{2})(n'' + \frac{1}{2})$  term is omitted.

Bands for which  $n'$  (or  $n''$ ) is constant and  $n''$  (or  $n'$ ) varies constitute an  $n''$  (or  $n'$ ) *progression*; thus the bands for which  $n'$ ,  $n''$  are respectively 0,0, 0,1, 0,2, 0,3... form the  $n''$  progression  $n' = 0$ , and the 0,2, 1,2, 2,2, 3,2... bands form the  $n'$  progression  $n'' = 2$ . Bands for which the change  $n'' - n'$  is constant form a *sequence*; thus the  $n'' - n' = +1$  sequence consists of the 0,1, 1,2, 2,3, 3,4... bands. In analysing a system it is usually expedient to arrange the wave numbers of the heads in a table such that the 0,0 band appears in, say, the left-hand top corner, each  $n''$  progression runs horizontally, each  $n'$  progression runs vertically and each sequence runs diagonally from top-left to bottom-right\*. The vibrational quantum analysis may indeed be said to consist of the correct construction of such a table, for when this is achieved, the values of  $n'$  and  $n''$  can be assigned with almost complete certainty, and the coefficients in equation (8) evaluated.

Criteria for the  $n'n''$  assignments are:

(i)  $\nu$  increases with decreasing  $n''$  in an  $n''$  progression and with increasing  $n'$  in an  $n'$  progression.

(ii) The intervals  $\Delta\nu$  between successive bands of a progression decrease with increasing  $n'$  or increasing  $n''$ , very nearly in arithmetical progression if  $Q$  heads or band-origins are tabulated, and less nearly in arithmetical progression if  $R$  or  $P$  heads are used.

(iii) A decrease of  $I$  is accompanied by an increase of  $\omega_0$ , and *vice versa*; hence, if the bands degrade towards the infra-red,  $I'' < I'$ ,  $\omega_0'' > \omega_0'$ , and above the intervals  $\Delta\nu$  are larger in an  $n''$  progression than in an  $n'$  progression; the reverse is true if the bands degrade towards the ultra-violet.

\* Table 3 on p. 524 is an example, the perusal of which will help to make clear the present statements; it is, however, a composite table in which, for economy of space,  $R$  head data appear immediately above  $Q$  head data for a rather extensive band-system.

(iv) As a consequence of (i) and (iii), along a sequence  $n'$  and  $n''$  increase in the direction in which the bands degrade.

(v) When the directions of increase of  $n'$  and  $n''$  are thus settled, their values are decided by the sudden cessation of an  $n''$  progression (say  $n' = 0$  or  $1$ ) at its low- $\nu$  end, and of an  $n'$  progression (say  $n'' = 0$  or  $1$ ) at its high- $\nu$  end; the test is applied by verification of the entire absence from the spectrogram of bands whose  $\nu\nu$  are obtained by extrapolations beyond the top row and left-hand columns of the above table.

(vi) If the bands have measurable  $Q$  heads, in bands degraded to the red the interval  $\nu_{R\text{head}} - \nu_{Q\text{head}}$  increases with diminishing  $n'$  along an  $n'$  progression and with increasing  $n''$  along an  $n''$  progression, and in bands degraded to the violet  $\nu_{Q\text{head}} - \nu_{P\text{head}}$  decreases in these directions. These facts, which follow from equations (6) and (7), are more useful in the recognition of  $Q$  heads than as evidence for the  $n', n''$  assignment.

(vii) The distribution of intensity amongst the bands of a system is normally of the type in which a progression (say  $n' = 4$  or  $n'' = 4$ ) has two intensity maxima separated by a minimum, and the locus of all the maxima is a curve of nearly parabolic form (the Franck-Condon parabola) such that (a) its axis approximately coincides with the  $0, 0$  sequence, and represents a rapid decline of intensity from a maximum to zero; (b) if the change  $I'' - I'$  or  $\omega_0'' - \omega_0'$  is very small, its vertex coincides with the  $0, 0$  band (which is the strongest of the system), and its two limbs are close to one another and to the  $0, 0$  sequence (which is the strongest, if not the only, sequence present); (c) as the change  $I'' - I'$  or  $\omega_0'' - \omega_0'$  increases, the vertex of the curve recedes from the  $0, 0$  band, and the limbs of the curve become wider apart; thus the wide curve of maxima which characterises a large change cuts the  $0$  sequence not at the  $0, 0$  band, but at a higher  $n', n''$  band.

(viii) The vibrational isotope effect, if present and precisely measurable, furnishes an absolute check on the  $n', n''$  numeration and is, in fact, the experimental evidence for the use of  $(n + \frac{1}{2})$  instead of  $n$  in the vibrational energy terms in equations (2), (3) and (8).

As a result of the analysis of different band-systems of the same molecule, and as a demonstration of the Ritz combination principle as applied to band spectra, it is frequently found that a given electronic level (recognised usually by its associated vibrational energies, and less often by the moment of inertia  $I_0$  and internuclear distance  $r_0$  for that state) is involved in two or more systems, either as a common initial state, or as a common final state, or as the initial state for one system and the final for another. Thus, in the "red" and "violet" systems of CN, the band-origin equations (3) have common values of  $\omega_0''$  and  $\omega_0''x''$ , indicating that the final electronic state for each system has a common set of vibrational energy levels. In the spectrum of CO there are about nine systems involving only eleven electronic states, the final state for the visible Ångström system, for instance, being both the initial state for the extensive ultra-violet "4th positive" system and also the final

state for another system; while for  $\text{CO}^+$  (as also for  $\text{B}^{11}\text{O}$  and  $\text{B}^{10}\text{O}$ ) there are three known systems with only three electronic states. In spectra containing many known systems, e.g.  $\text{H}_2$  and  $\text{He}_2$ , the system-origins form *series* of the Rydberg-Ritz type already well known in atomic line spectra.

A certain correspondence exists between the spectra and electronic states of many of the lighter molecules and those of the atoms containing two less extra-nuclear electrons, and it is inferred that in the molecule each atom retains its own  $K$  electrons, while the remaining electrons form an outer configuration similar to that in the comparable atom. Thus corresponding to the 11-electron atom Na, which has 2  $K$ , 8  $L$  and 1  $M$  electrons, each of the 13-electron molecules  $\text{BeF}$ ,  $\text{BO}$ ,  $\text{CN}$ ,  $\text{CO}^+$ ,  $\text{N}_2^+$  contains, besides its 2 + 2  $K$  electrons, 9 outer electrons which are regarded as an outer structure of a group of 8 electrons, together with 1 outermost or valence electron. Similarly, the 21-electron molecules  $\text{MgF}$ ,  $\text{AlO}$ ,  $\text{SiN}$ , have, like the 19-electron atom K, 8 + 8 + 1 electrons outside the  $K$  electrons and the nuclei, and are thus also "one-valence-electron" molecules. Again,  $\text{CO}$  and  $\text{N}_2$  (14 electrons) are, by comparison with  $\text{Mg}$  (12), "two-valence-electron" molecules\*.

Aided by this correspondence, detailed theoretical study of the fine structure of bands of different types has led to the classification of molecular electronic levels into singlet, doublet, triplet, . . . levels, and into types which are to some extent analogous to the term-types  $S$ ,  $P$ ,  $D$ ,  $F$  already known in atomic spectra. As in the case of atoms, the electronic levels of odd and even molecules have even and odd multiplicities respectively. The molecular electronic levels were until recently designated by the same capital letters, but it is sometimes necessary to discuss the electronic levels of molecules in relation to those of their constituent atoms, and to avoid confusion the above letters are now reserved for atomic levels, and  $\Sigma$ ,  $\Pi$ ,  $\Delta$ ,  $\Phi$  are used for molecular levels.

This new notation also serves to emphasise the fact that the electronic levels in the two cases are not completely analogous. While transitions between similar states, e.g.  $S \rightarrow S$ ,  $P \rightarrow P$ , are never found in atomic spectra, such transitions as  $\Sigma \rightarrow \Sigma$ ,  $\Pi \rightarrow \Pi$ , are frequently represented in molecular spectra. Thus, the normal and lowest two excited states are  $^2S$ ,  $^2P$ ,  $^2S$  respectively for Na (11) and K (19), and  $^2\Sigma$ ,  $^2\Pi$ ,  $^2\Sigma$  respectively for the 13-electron and 21-electron molecules already mentioned; and in the  $\text{CN}$  spectrum, for instance, the "red" system is attributed to the transition  $^2\Pi \rightarrow ^2\Sigma$ , and corresponds to the Na yellow doublet  $^2P \rightarrow ^2S$ , while the "violet" system is due to  $^2\Sigma \rightarrow ^2\Sigma$  (the final state being, as for the "red" system, the normal  $^2\Sigma$  state) and has no corresponding line  $^2S \rightarrow ^2S$  in the Na spectrum. Again, three band-systems which are well known in laboratory and stellar spectroscopy, namely, the "2nd positive" of  $\text{N}_2$ , the Swan system of  $\text{C}_2$  and the blue-green (Antarian) system of  $\text{TiO}$ , are each attributed to a transition  $^3\Pi \rightarrow ^3\Pi$ , which has no counterpart  $^3P \rightarrow ^3P$  in atomic spectra.

\* A note on heavier oxides and their comparable atoms appears in a footnote on p. 531, *q.v.*

## DISCUSSION

MR J. H. AWBERY: I should like to thank Dr Jevons for his very clear introduction to the general subject of band spectra. I think I must be expressing the opinions of many others when I say that I am interested generally in "modern physics," although my active work lies in other directions; for those in this position there have been ample opportunities to read about the results and ideas of line spectroscopy, but our knowledge of band spectra has been limited to the facts that these spectra have been found to exhibit regularities, and that moments of inertia of the molecules could be estimated by means of them. The literature of the subject is very technical, and without some such survey as Dr Jevons has now provided, we lacked that substratum of knowledge which was necessary before more detailed accounts could be profitably studied. I should like to know more of the calculation of the function by which the rotational energy of the molecule is expressed in terms of the quantum number  $j$ . The forms quoted are identical with those obtained for the free rotator\*, and it is stated that much more complicated forms are sometimes necessary. I suppose this refers, at any rate in part, to the fact that a molecule does not consist of two mass-points only. In terms of Bohr's picture, there may be orbits of various degrees of eccentricity, and these would make the simple expressions inapplicable. Perhaps Dr Jevons would correct me if this is wrong, and also give a few references either to summaries or to the most important papers which would enable me, and others in the same stages of ignorance, to lighten our darkness.

AUTHOR'S reply: In my brief outline I have made no attempt to indicate methods of determining the rotational energy expression from the fine structure analysis of the bands. For such information I would refer Mr Awbery to the National Research Council's *Bulletin* no. 57 on "Molecular Spectra in Gases," pp. 142-177. The rotational energy expression  $Bj(j+1)$  of the new mechanics was obtained and developed by Dennison, *Phys. Rev.* **28**, 318 (1926), Kronig and Rabi, *Nature*, **118**, 805 (1926), and *Phys. Rev.* **29**, 262 (1927), and Reiche, *Z. f. Phys.* **39**, 444 (1926).

\* For example, by Schrodinger: *Collected Papers on Wave Mechanics*, p. 35.



# THE RELATION BETWEEN HYDROGEN PRESSURE AND FILAMENT RESISTANCE IN A TUBE CONTAINING GLOWING TUNGSTEN

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**ABSTRACT.** When a tungsten filament in a tube containing hydrogen is caused to glow, the gas rapidly disappears while the resistance of the filament rises progressively. The latter phenomenon can be used to measure the pressure of the hydrogen. It is suggested that chemical action takes place between the hydrogen and tungsten.

## § 1. INTRODUCTORY

IN the course of preliminary experiments begun some time ago on the thermionic emission of tungsten in an atmosphere of hydrogen, it was found difficult to carry out accurate measurements, owing to the rapid disappearance of hydrogen in the tube. At the same time it was noted that the resistance of the filament increased. It was thought that this effect was probably due to lessened conduction and convection through the film of gas, and that the increase of resistance might be used to measure the pressure of the hydrogen, somewhat after the manner of the Pirani-Hale gauge, in which, however, wires are used at a much lower temperature.

In § 2 of this paper it is shown that the variations of the resistance of an electrically heated tungsten filament, glowing at high temperature in an atmosphere of hydrogen, can be used as a measure of the pressure of the hydrogen in the tube. In § 3 this method is applied to observations on the disappearance of hydrogen in the thermionic tube.

## § 2. RELATION BETWEEN FILAMENT RESISTANCE AND HYDROGEN PRESSURE

*Theory.* In the case of an electrically heated tungsten filament in an atmosphere of hydrogen the rate of loss of energy is equal to the input in watts, on the assumption that a steady state has been reached and that the loss of heat through the ends is negligible.

The heat is lost in two ways\*:

(i) By radiation. The radiating power  $\propto T^\omega$ , where  $\omega$  is a constant, taken as 4. The loss therefore  $= \sigma (T^4 - T_0^4)$ , where  $T$  and  $T_0$  are the absolute temperatures of the surface and surroundings and  $\sigma$  is a constant.

\* It is assumed that at the temperatures (namely 1300° and 1800° absolute) and pressures dealt with in these experiments the loss of heat caused by the dissociation of the hydrogen into atoms can be neglected compared with the conduction, convection and radiation losses.

(ii) By conduction and convection through the film of gas. When a stationary film of gas is in contact with any hot object at high temperatures, free convection consists essentially of conduction through the film and can be calculated by the laws of conduction. Therefore if two surfaces at an infinitely small distance apart  $dx$  differ in temperature by  $dT$ , the rate of loss of heat,

$$Q = KA \, dt/dx,$$

where  $K$  is the thermal conductivity of the medium, between the surfaces, and  $A$  the area. Hence, for isothermal surfaces at a finite distance apart,

$$Q = \int K dT / \int \frac{dx}{A}.$$

Taking the conductivity  $K$  as a known function of the temperature, the value of  $\int K dT$  becomes the product of the conductivity for the mean temperature of the surfaces and the temperature difference between them.

Let the space factor  $\int \frac{dx}{A}$  be denoted by  $s$ . If the wire and the surrounding film of gas be considered as a cylinder and cylindrical shell, the space factor

$$s = 2\pi l / \log_e (b/a),$$

where  $a$  and  $b$  are the internal and external radii of the film and  $l$  is the length.

Therefore if  $T$  is the temperature of the wire, and  $T_0$  the temperature at the outer surface of the film, the loss  $W$  in watts per unit length

$$= \frac{2\pi \times 4.2}{\log_e (b/a)} \int_{T_0}^T K dT.$$

Since  $s$ , the space factor per unit length,  $= 2\pi / \log_e (b/a)$ , the watts lost per unit length by conduction and convection  $= s (\Phi_1 - \Phi_2)$ , where

$$\Phi_1 = 4.2KT,$$

and

$$\Phi_2 = 4.2KT_0.$$

The watts lost per unit length by radiation

$$= \sigma\pi a (T^4 - T_0^4),$$

and the watts input per unit length

$$= RI^2/l,$$

where  $I$  denotes current in the wire.

Assume that  $T_0^4$  and  $s\Phi_2$  can be neglected compared with the  $T$  terms, and to a first approximation let  $k$  be the average value of  $4.2 K$ .

Then

$$RI^2/l = \sigma\pi a T^4 + s\Phi_1.$$

Taking the resistance to be approximately proportional to the absolute temperature, let  $T = CR$ , where  $C$  is a constant.

Then

$$RI^2/l = \sigma\pi a C^4 R^4 + skCR,$$

$$I^2/l = \sigma C^4 R^3 \pi a + skC$$

.....(1).

Let  $R_0$  be the resistance when the pressure is 0, and there are no conduction or convection losses through the film of gas.

$$\begin{aligned} \text{Then} \quad R_0 I^2 / l &= \sigma \pi a C^4 R_0^4, \\ I^2 / \sigma \pi a l C^4 &= R_0^3 \end{aligned} \quad \dots\dots(2).$$

$$\begin{aligned} \text{From (1)} \quad (I^2 / l - s k C) / \sigma \pi a l C^4 &= R^3 = (R_0 + \Delta R)^3, \\ \text{where} \quad \Delta R &= \partial R / \partial P \cdot \Delta P. \end{aligned}$$

$$\begin{aligned} \text{Hence} \quad (I^2 - s l k C) / \sigma \pi a l C^4 &= R_0^3 + 3 R_0^2 \Delta R + \dots \\ \text{or} \quad - s l k C / \sigma \pi a l C^4 &= 3 R_0^2 \Delta R \end{aligned} \quad \dots\dots(3),$$

terms in  $\Delta R^2$  and  $\Delta R^3$  being neglected.

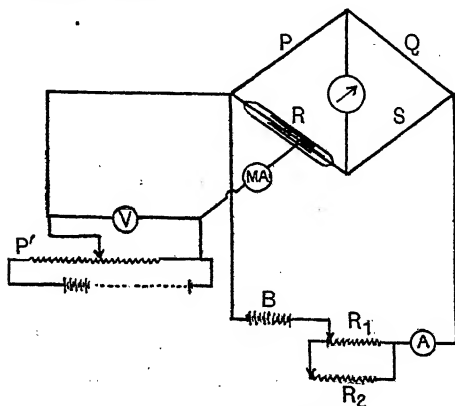


Fig. 1. Circuit diagram.

P, Q, R, S, arms of Wheatstone bridge; B, battery in bridge circuit for heating current;  $R_1$ ,  $R_2$ , resistances, large and small, placed in parallel for final adjustment of current; P', high resistance rheostat with dry battery of 120 volts; V, voltmeter; MA, microammeter.

Divide (3) by (2), so that

$$- s l k C / 3 I^2 = \Delta R / R_0,$$

on the assumption that  $k$  is independent of the pressure, and that  $s$  is constant for equal increases of pressure.

$$\text{Then} \quad \Delta R / R_0 \propto 1 / I^2,$$

$$\text{or} \quad \Delta R / R_0 \times I^2 = K,$$

where  $K$  is a constant.

*Method of investigation.* The tube used in the experiments was a diode, cylindrical in shape. A tungsten filament, welded to thick leads, was stretched along the axis of a cylindrical copper anode. The dimensions were:

Length of tungsten filament	...	7.5 cm.
Diameter of tungsten filament	...	0.012 cm.
Length of anode cylinder	...	20 cm.
Diameter of anode cylinder	...	2 cm.

The tube was connected to (1) a Geissler tube, (2) a liquid air trap, (3) an  $\text{H}_2\text{SO}_4$  gauge, in which pressures could be read to 0.1 mm. of  $\text{H}_2\text{SO}_4$  (= 0.14 mm. of

mercury) by means of a travelling microscope, (4) a tube containing coco-nut charcoal for immersing in liquid air, (5) a Geryk pump for preliminary evacuation of the apparatus. The apparatus was placed in an oven and the occluded gas baked out by preliminary and prolonged pumping and heating. The hydrogen was introduced through a heated palladium tube.

*Electrical arrangements.* The filament  $R$  and a compensating low resistance  $S$  were placed in the adjacent arms of a Wheatstone bridge. The arrangement of apparatus is shown in Fig. 1. The arm  $Q$  was 2000 ohms, and  $P$  varied with  $R$ .

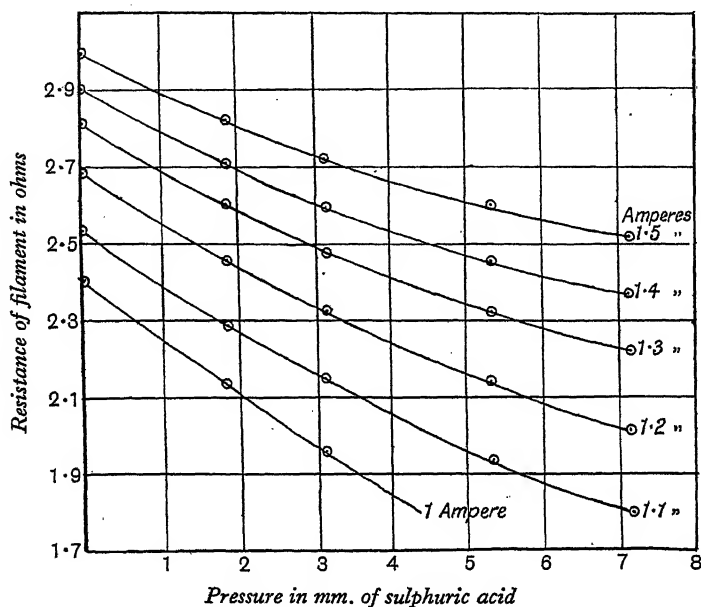


Fig. 2. Typical series of resistance-pressure curves for varying values of the heating current.

*Results.* Fig. 2 shows a typical series of resistance/pressure curves. There were many series taken, with four filaments, and in every case the permanent increase in resistance was noted, though the value of  $\Delta R/R_0$  for equal increases of pressure did not alter for a constant heating current. Values of  $\Delta R/R_0$  for equal increases of pressure  $\Delta p$  are given below for varying values of the heating current, the values of  $\Delta R/R_0$  being calculated from series of graphs of which Fig. 2 is an example.

$I$	1.5	1.4	1.3	1.2	1.1
$\Delta R/R_0$	0.045 0.056 0.042 0.058 0.045 0.048 0.062 0.058	0.054 0.049 0.061 0.07 0.056 0.051 0.066 0.061	0.061 0.081 0.052 0.069 0.07 0.06 0.06 0.077	0.072 0.09 0.072 0.076 0.073 0.07 0.069 0.082	0.082 0.096 0.092 0.09 0.087 0.091 0.09 0.092
Mean	0.052	0.059	0.066	0.076	0.091

Fig. 3 gives the values of  $\Delta R/R_0$  plotted against  $1/I^2$ , showing that  $\Delta R/R_0 = K/I^2$ , from which  $K = 0.107$ .

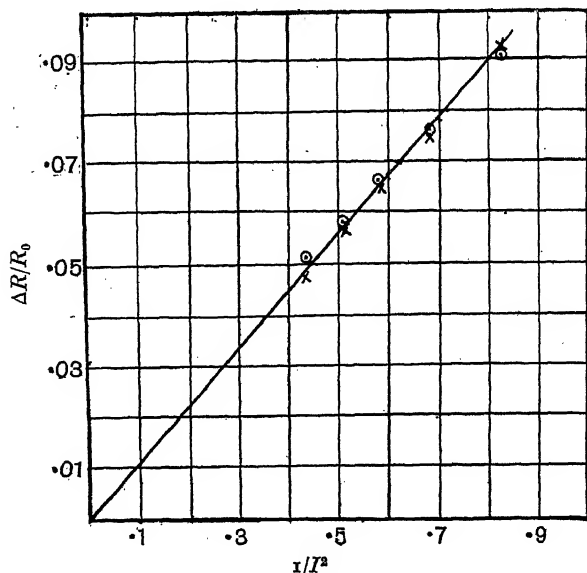


Fig. 3. Relation between resistance increments and the heating current.  
Calculated  $\times \times \times$ . Observed  $o o o$ .

### § 3. OBSERVATIONS ON THE DISAPPEARANCE OF HYDROGEN IN THE THERMIONIC TUBE

The disappearance of gas in the discharge tube has been studied extensively, and this effect was very marked in the type of tube used for these experiments. It was therefore thought that the tungsten filament glowing at a high temperature in an atmosphere of hydrogen could itself be used as a pressure gauge of the Pirani-Hale type, as described in § 2. This method was chosen because it was necessary to keep the heating current constant for the purposes of the measurement of the electronic emission.

Many attempts were made to get satisfactory and consistent readings of the thermionic currents, at various pressures, when the voltage applied between filament and anode was slowly increased. The difficulties that were encountered suggested this part of the investigation, in which the rate of increase of resistance of the filament, owing to the diminished cooling effect due to the disappearance of hydrogen, could be used as an indication of the pressure. This method would do away with the necessity for any other type of gauge, which would be an advantage when it is advisable to avoid any trace of the mercury vapour from a McLeod gauge.

It was carefully observed that: (i) There was no increase of resistance of the fila-

ment with time at high temperatures, before the introduction of the hydrogen, or after the total disappearance of the hydrogen. (ii) The pressure of the hydrogen in the tube remained constant if the filament was not glowing brightly. (iii) The application of a potential difference between filament and anode did not alter the rates of increase of resistance of the filament, or of the disappearance of the hydrogen.

The gradual permanent increase in the resistance of the filament, which in the experiment was from  $\cdot 62$  to  $\cdot 92$  ohm, is shown in both parts, and it is suggested in the discussion that there may be chemical action between the hydrogen and the hot tungsten.

*Experimental procedure.* The thermionic tube was similar to that used in § 2, while the electrical arrangements were slightly modified by the introduction of a rotating electrically driven commutator. This was arranged in such a way that there was no heating current flowing in the circuit when a voltage was applied between filament and anode. This was done to avoid the effects due to the drop of

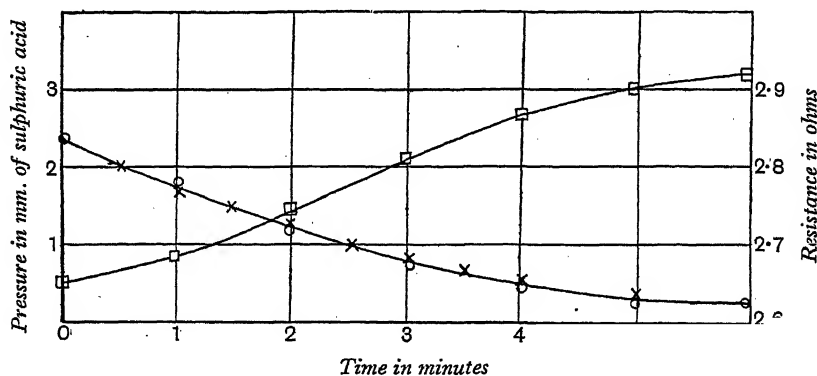


Fig. 4. Observed values of pressures  $\circ$ — $\circ$ — $\circ$ .  
Calculated values of pressure  $\times$ — $\times$ — $\times$ .  
Resistance of filament  $\square$ — $\square$ — $\square$ .

potential along the wire, the current and the application of the voltage between filament and anode being alternately intermittent. Hydrogen was introduced into the apparatus by heating the palladium tube, and the heating current was then increased till the filament was glowing brightly.

The temperatures given were deduced from the change of resistance of the filament by the use of data given by Langmuir (1).

Alternate readings were then taken of the resistance of the filament and the pressure of the hydrogen as shown on the sulphuric acid gauge.

It is shown in § 2 that  $I^2 \Delta R / R_0 = K$ , where  $K = \cdot 107$ . Thus for any experimental readings of  $\Delta R / R_0$  for a known value of  $I^2$ ,  $\Delta p$  can be calculated. Values of  $p$  were therefore deduced for any given value of the resistance of the filament.

Fig. 4 shows the increase of resistance with time, and the same figure shows the values of the pressure as observed on the sulphuric acid gauge together with those

calculated as above. These are found to be in good agreement. This is shown more clearly in Fig. 5, where the results are recorded as resistance/pressure curves.

It is therefore concluded that the method proposed for estimating the hydrogen pressure by observations of the filament resistance is, for the small range of pressures studied, satisfactory.

#### § 4. DISCUSSION OF RESULTS

It has been shown that a measurement of the pressure of a gas in a thermionic tube containing a tungsten filament can be made from direct observations of the resistance of the filament, if the latter is heated to high temperatures in an atmosphere of hydrogen. This method is independent of the gradual permanent increase of the resistance of the filament, so that there is no necessity for repeated calibrations of the pressure gauge.

The permanent increase may be due to the sputtering of the cathode, to the action of traces of water vapour, or to some chemical action between the heated tungsten and the hydrogen. Calculations showed that the increase was too great to be accounted for by cathodic sputtering, and care was taken to avoid the effects of any traces of water vapour. This was done by the alternate heating and cooling by liquid air of the tube containing charcoal, which was placed between the thermionic tube and the sulphuric acid gauge. The third of the foregoing explanations was suggested because of the rapid disappearance of the hydrogen when the filament was raised to a high temperature, whereas little or no effect was observed when the filament was not glowing.

In support of the suggestion that there was a chemical action, the following rough calculation is given of the total masses of tungsten and hydrogen disappearing in the course of the experiment:

Initial mass of filament	= 0.02 gm.
Final mass of filament	= 0.014 gm.
Loss in mass	= 0.006 gm. = $m_1$ .
Loss in mass of hydrogen	= 0.000063 gm. = $m_2$ .

(Calculated from volume of vessel and gas laws.)

Therefore  $m_1/m_2 = (\text{mass of tungsten})/(\text{mass of hydrogen}) = 97/1$ .

This approximation suggests that there may be chemical action between the tungsten (atomic weight 184) and hydrogen, a compound with empirical formula  $H_2W$  being formed.

Investigations on the disintegration of a tungsten cathode in an atmosphere of hydrogen have however shown<sup>(2)</sup> that it is small compared with that which occurs

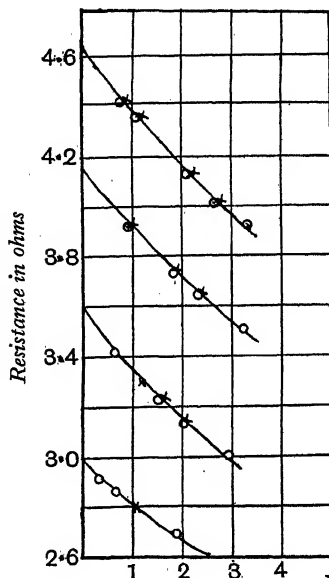


Fig. 5. Calculated and observed values shown as resistance pressure curves.

in other gases, and is anomalous; while Dushman (3) states that investigators have observed that hydrogen is absorbed by tungsten to a negligible extent.

Stead and Trevelyan (4) suggest that hydrogen acts on the filament to form an endothermic compound stable at high temperatures, and the General Electric Co. Research Staff (5) show that if hydrogen is present it should disappear in the presence of hot tungsten without ionisation by a field.

Langmuir (6), in his extensive work on the subject, showed that hydrogen would disappear even without the passage of a discharge. He found that hydrogen could be dissociated by tungsten and other metallic wires when the temperature of the metal was raised above  $1300^{\circ}$  absolute and that the disappearance is due to the dissociation of the hydrogen into atoms which condense on the walls, but that the observed decrease of pressure corresponds only to  $1/7$  or less of the amount actually dissociated. There is a marked increase above  $2500^{\circ}$  absolute.

Congdon (7) mentions the peculiar behaviour of hot tungsten in the presence of hydrogen. It is noteworthy that many experimenters, when working with hydrogen, avoid the use of a tungsten cathode.

#### § 5. SUMMARY OF CONCLUSIONS

It has been shown in this paper:

- (i) That in an electrical manometer, if the heating current is kept constant, the relative diminution of resistance with pressure varies as the square of the heating current.
- (ii) That this principle may be applied to the deduction of values of the pressure of hydrogen in a tube, by readings of the resistance of the tungsten filament, which increases owing to the disappearance of the hydrogen.
- (iii) That the permanent increase of the resistance may be due to the action of the hydrogen on the hot tungsten.

#### § 6. ACKNOWLEDGMENTS

In conclusion I should like to express my thanks to Professor Richardson for his helpful criticism and advice and for allowing me to work in his laboratories. I should also like to thank Dr W. A. Leyshon for her help and constructive suggestions.

#### REFERENCES

- (1) Langmuir, *Phys. Rev.* **7**, 3 (1916).
- (2) *Phil. Mag. G.E.C. Staff*, **45**, 98 (1923).
- (3) Dushman, "High Vacuum. Theory of Adsorption at Low Pressures."
- (4) *Phil. Mag.* **287**, 978 (1924).
- (5) *Trans. Faraday Soc. G.E.C. Staff*, **17**, 485 (1922).
- (6) *Journ. American Chem. Soc.* **37**, 1161 (1915).
- (7) *Phil. Mag.* **47**, 458 (1924).



## DISCUSSION

Mr N. L. HARRIS: While congratulating the author upon the results she has obtained by using this method of pressure measurement, I suggest that some modifications should be made in designing a practical gauge on these lines. The temperature scale of tungsten has been revised several times since 1912, with corresponding revision of its specific properties as functions of temperature: the latest and most complete information is to be found in that given by Jones and Langmuir\*. It is not clear (p. 547) that  $s\Phi_2$  is negligible compared with  $s\Phi_1$ . Over the range of temperature used, the expression  $T = CR$  should be replaced by  $T = 3.24 \cdot 10^7 \rho \times 192$ , where  $\rho$  is the resistivity of tungsten in ohm/cm. At  $1500^\circ$  the constant term amounts to some 15 per cent. of the whole and must then enter the equations in the fourth power, with the possibility that even over small temperature ranges the end expression in  $\Delta R$  may need modification. A filament as thick as 0.012 cm. in diameter and only 7.5 cm. long suffers badly from "end effects" when running at  $1500^\circ$ , in fact only a central few millimetres are at a uniform temperature†. The entry of gas into the tube will modify the temperature distribution and change the overall resistance apart from the main effect we are studying. Unless the "ends" are short to start with, the effect may be serious: I suggest wire about 0.0025 cm. in diameter as more suitable. Again, traces of oxidising vapours may change the thermal emissivity of the wire by large amounts as surface oxide layers form, and vapours of hydrocarbons are capable of carbonising the tungsten at  $1600^\circ$ ‡. In both cases the change in resistance of the wire for constant heating current may be large. A trace of water vapour or carbon dioxide thins a hot tungsten wire considerably in cyclic reactions. Perhaps the presence of the tap between the liquid air trap and the hot filament, in the apparatus described, accounts in these ways for some of the effects mentioned in the latter part of the paper.

Dr M. C. JOHNSON: Some time ago I had occasion to consider the relative magnitude, under certain conditions, of the various factors contributing to this change of resistance of a hot tungsten wire in hydrogen. The classification of a few of these factors may be of interest to those reading the paper, to which all workers *in vacuo* are indebted for its careful and thoroughgoing attainment of consistency in a very complex problem.

1. *Changes of resistance due to cooling of wire by gas.* (a) Change in composition of gas mixture whose components are differentially conducting. (I should like to be assured that this is negligible in the present work. The partial pressure of  $H_1$  in the  $H_2$  must be considerable when emission is going on at certain pressures.) (b) Diffusion away from the wire of  $H_1$  capable of giving up heat of recombination. (Did the author find any trace of this at her highest temperatures?) (c) Simple change of total pressure.

\* *General Electric Review*, 30, 310 (1927).

† Worthing, *Journ. Frank. Inst.* 194, 597 (1922).

‡ Andrews, *Journ. Phys. Chem.* 27, 270 (1923).

2. *Changes of resistance due to altered composition of wire.* If the wire were not initially free from oxide this would gradually disappear in the hydrogen. The author has carefully eliminated water vapour: would this act simply by oxidation, if present? Her deduction of a definite compound  $(H_2W)_x$  is an important advance on the usual vague assumption that these substances do not react. Will this reaction reverse at the highest temperatures? Is there any sign of solution of the hydrogen in the tungsten?

3. *Changes of resistance due to liberation of heat at gas-solid interface.* Any  $H_1$  dissociated by electron impact may communicate  $10^5$  cal./gm.-mol. in catalytic recombination at the tungsten surface. Cold tungsten wires can be made white hot by insertion in a stream of partially dissociated  $H$ . I have had occasion to wonder before whether this, or the heat of adsorption (which I think can reach  $10^4$  cal.), will not affect resistance considerably. Presumably there is some temperature at which the Langmuir cooling effect is balanced by such heating effects. Can the author give any advice as to this?

I should also be grateful if the author can give any advice as to whether it is possible to know—from “fatigue” effects for example—how much of the “lost” hydrogen goes to the tungsten and how much to the glass walls.

AUTHOR'S reply: I should like to thank Mr Harris and Dr Johnson for their criticisms and suggestions, but should point out that the method of pressure measurement described in my paper is not recommended as a practical form of gauge. I felt that the point of interest was the fact that, during a long course of experiments, it was possible to make simple and accurate estimations of the pressure of hydrogen by the variations in the electrical resistance of the tungsten filament, even though chemical changes might be taking place. If the object had been to design a practical form of gauge a shorter wire of smaller diameter would have been used to avoid the irregularity of temperature distribution and the end losses. It was not necessary, for the purposes of the experiment, to have an exact knowledge of the temperature, and the values given were calculated from Langmuir's original tables merely to indicate the range of temperature through which the filament was heated. It was assumed that, in general,  $s\Phi_2$  could be neglected compared with  $s\Phi_1$ , if the filament were raised to a high temperature. The fourth power term applies to the radiation, and it is known that the heat lost in this way is small compared with the conduction and convection losses.

There is the possibility that any hydrocarbon vapour will react with incandescent tungsten to form tungsten carbides. A spectroscopic examination of the gas in the tube, however, showed only hydrogen lines and bands, though this could not be taken as a proof of the entire absence of carbon.

At the temperature given, it seems unlikely that the results would be affected by the loss of heat due to the change in the composition of the gas. It is well known that when a hot cathode is employed there will be only a slight amount of thermal dissociation of  $H$ , even with a wire operated at  $2500^\circ$  C. At the highest temperature used in my experiments the results showed none of those irregularities that would

be consequent upon the abnormally high conductivity brought about by the hydrogen atoms diffusing into the colder gas, and, on re-combining, giving up the heat of reaction.

I have had no opportunity of studying the problem from the chemical standpoint and cannot, therefore, give any information on this subject, though it seems probable that the heat of adsorption would affect the resistance. It was not possible to find out how much of the lost gas went to the walls, and how much to the filament. I assumed in my approximate calculation that all the gas which disappeared combined with the tungsten. There was no darkening of the glass of the tube, nor was there any return of pressure after the hydrogen had disappeared.

All the effects that have been mentioned may play a part in the variation of the resistance, yet the facility and accuracy with which I was able to calculate the pressure led me to suggest that the simple explanation which I have offered seems justified by the consistent results of repeated experiments.

# THE BAND SYSTEMS OF TITANIUM OXIDE

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**ABSTRACT.** (i) The bands of TiO have been found to extend toward the infra-red through some 800 Å further than the range previously known. (ii) Bands in the orange, red and infra-red regions have been analysed into two systems, distinct from the blue-green system. One of these is due to the transition  ${}^1\Pi \rightarrow {}^1\Sigma$ , the other to  ${}^3\Sigma \rightarrow {}^3\Pi$ , the latter having the same final energy level as the blue-green system  ${}^3\Pi \rightarrow {}^3\Pi$ . (iii) Analysis of other bands in the red is in progress.

## § 1. INTRODUCTION

IN 1904 and 1907 Prof. A. Fowler\* published his investigations on the origin of the bands characteristic of the M-type stars and showed that they arose from an oxide of titanium; he photographed the spectrum and measured the heads, sub-heads and maxima of the bands from  $\lambda 4350$  to  $\lambda 7200$ . Numerous investigations of these bands in their relation to stellar phenomena have appeared during many years, but little has yet been published on the analysis of their gross and fine structure†, ‡, §, ||. The plate accompanying Prof. Fowler's second paper shows that all the bands are degraded toward the red, but it exhibits a distinct difference in structure between the bands in the region from the violet to green and those in the region from the orange to the infra-red. In 1922–1923 the author re-photographed the spectrum from  $\lambda 5950$  to  $\lambda 4000$  in the second order of the 10 ft. grating of the Imperial College of Science, the prime object at the time being the solution of a problem in stellar spectroscopy¶. By the use of an iron arc fed with titanium dioxide, it was found that the banded structure extended to about  $\lambda 4000$ , but had no well-defined heads of wave-length shorter than  $\lambda 4205$ . Publication of these spectrograms was postponed while analysis of the fine structure was in progress. In 1926 A. S. King\*\*, using the electric furnace and passing a strong current of oxygen through a graphite tube containing titanium, also found that the banded structure extended to about  $\lambda 4025$ ; with the aid of a registering microphotometer he determined the wave-lengths of ten maxima, most of which he considered to be probable band heads.

Birge and Christy having analysed three bands in the blue-green region, namely, the (1, 0), (0, 0) and (0, 1), investigation of the red and infra-red region seemed to be of next importance.

\* *Roy. Soc. Proc. A*, 73, 219 (1904); 79, 509 (1907).

† Fiebig, *Z. wiss. Phot.* 8, 73 (1910).

‡ Eder and Valenta, *Wien. Ber.* 119, 37 (1910).

§ Birge and Christy, *Phys. Rev.* 29, 212 (1927), (abstract); *Nature*, 122, 205 (1928).

|| Christy, Thesis, in the press.

¶ Frost and Lowater, *Astrophys. J.* 58, 265 (1923).

\*\* *Publ. Astron. Soc. Pac.* 38, 173 (1926).

## § 2. EXPERIMENTAL PROCEDURE

The source used was a Pfund iron arc supplied with an extra radiator and fed with titanium dioxide. The spectrum was photographed by means of a spectrograph of the Littrow type, having a dense glass prism of  $30^\circ$ , of which the dispersion ranged from 8.6 Å/mm. at  $\lambda$  5600 to 35.5 Å/mm. at  $\lambda$  8700. Spectrograms were taken with sensitised kryptocyanine and neo-cyanine plates from  $\lambda$  5500 to  $\lambda$  8800; panchromatic plates were also used in order to obtain a truer estimate of the intensity of the bands by taking into account the sensitivity of the three kinds of plates.

Measurements of the heads were made in the usual manner, the wave-lengths being referred to those of iron lines recommended as secondaries by the International Astronomical Union\* wherever available, otherwise to wave-lengths published by Meggers and Kiess†. The numerous titanium lines occurring in this region were identified by the table of wave-lengths of Ti given by H. N. Russell‡.

The wave-length of the least refrangible head determined with certainty is 7996 Å; that of the least refrangible head hitherto recorded is 7197 Å (Fowler). Thus the bands have been found to extend through 800 Å further into the infra-red than the range previously known. Although spectrograms were continued through still another 800 Å into the infra-red, only one other possible head could be detected after elimination of the atomic Ti lines included in Russell's table.

## § 3. INTENSITY AND MULTIPLICITY

At first the distribution of intensity appears unusual, but vibrational analysis reveals the explanation of this appearance. Further, it will be observed from the plate that some heads appear to be double, others triple; and where they are merely double, the second head is much less strong than the first. Such double heads have the appearance of *R* and *Q* heads, but the data obtained from the difference in their wave-numbers§ do not give decisive proof of this. However, the assignment of the electronic transitions arrived at by analogy with the "comparable atom" requires *R* and *Q* heads; this point will be more fully discussed in a later section.

Four sequences in the region between  $\lambda$  6300 and  $\lambda$  8000 form a system of triplets, the *R* heads of which may be denoted by  $R_a$ ,  $R_b$ ,  $R_c$  or *a*, *b*, *c*, and the *Q*'s by  $Q_a$ ,  $Q_b$ ,  $Q_c$ ; the differences in the wave-number of these triplet heads of the (0, 0) band are  $R_a - R_b = 66.6$ ,  $R_b - R_c = 74.4$  cm.<sup>-1</sup>, while the *R* and *Q* separations are of the order of 11 cm.<sup>-1</sup>. The appearance of the narrowly spaced triple heads is produced by the proximity of the second head of the first member of the triplet sequence to the first head of the third member of the triplet, as for instance the  $R_a$  head of the (1, 1) band to the  $R_c$  head of the (0, 0) band. In

\* *Trans. Int. Astr. Union*, 3, Table 1 (1929).

† *Scientific Papers, Bur. Stan.* No. 479 (1924).

‡ *Astrophys. J.* 66, 347 (1927).

§ Jevons, *Roy. Soc. Proc. A*, 117, 351 (1928).

some cases such heads coincide and produce the effect of a distribution of intensity which appears quite anomalous.

In addition to this triplet system, a singlet system has been found in the orange; so far as it has yet been determined, it consists of one sequence only with its (0, 0) head at  $\lambda$  5597.85,  $\nu$  17859.1  $\text{cm}^{-1}$ . Here the  $R - Q$  separations are of the order of 19  $\text{cm}^{-1}$ .

The analysis of some thirty to forty other heads, not included in the singlet or triplet systems mentioned above, nor in the less refrangible portion of the blue-green system, is in progress.

#### § 4. OBSERVATIONAL DATA

In Table 1 are collected the data for the heads which have been found between  $\lambda$  5599 and  $\lambda$  8800, including some which belong to the blue-green system. Columns 1 and 2 contain the wave-lengths, intensities (in parentheses) and wave-numbers respectively. Column 3 contains the vibrational quantum numbers, with prefixed letters distinguishing the bands of different systems, and suffixed letters the members of the triplets:  $\alpha$  indicates members of the blue-green system, identified by the formula of Birge and Christy;  $\beta$  the  $R$  and  $Q$  heads of the singlet orange system; heads designated by  $\gamma$  belong to the red-infra-red system. Suffixes  $a$ ,  $b$ ,  $c$  indicate the first, second and third members of the triplet heads in the red-infra-red and blue-green systems. Heads with no quantum numbers assigned have not yet been completely analysed. Column 4,  $O - C$ , contains the differences between the observed wave-numbers and those calculated from equations (1) and (1') for the orange system  $\beta$ , from equation (2) for the red-infra-red system  $\gamma$ , and from Birge and Christy's formula for the blue-green system  $\alpha$ . Column 5,  $O - C$ , contains similar differences found from equation (3) for system  $\gamma$ .

All the  $R$  and  $Q$  heads so far identified of the singlet orange system  $\beta$  are included in the first ten lines of Table 1; they are put into the form of  $n'$  and  $n''$  progressions in Table 2 in order to exhibit the first differences between the members of the sequence. Since the system consists of a single (0) sequence only, no vibrational constants can be determined, but it can be represented by the following equation, where  $n = n' = n''$  and these symbols have integral values 0, 1, 2 ...:

$$\nu = \nu_e + (\omega_0' - \omega_0'')(n + \frac{1}{2}) - (\omega_0'x' - \omega_0''x'')(n + \frac{1}{2})^2,$$

which becomes for the  $R$  and  $Q$  heads, respectively,

$$\nu_R = 17909.04 - 99.54(n + \frac{1}{2}) - 0.302(n + \frac{1}{2})^2 \quad \dots\dots(1),$$

$$\nu_Q = 17890.06 - 99.58(n + \frac{1}{2}) - 0.257(n + \frac{1}{2})^2 \quad \dots\dots(1').$$

The vibrational analysis of the bands in the red-infra-red system  $\gamma$  is shown in Tables 3 and 4, which consist of the usual  $n'$  and  $n''$  progressions of  $R$  and  $Q$  heads respectively; they are arranged in triple form to demonstrate the consistency of the triplets. From the data in Table 3 equations (2) and (3) have been deduced, the coefficients of  $(n' + \frac{1}{2})$  and  $(n'' + \frac{1}{2})$  giving the vibrational frequency of the rotationless molecule in the initial and final states respectively.

Table 1. Heads of bands of TiO

$\lambda$ (air)	$\nu$ (vac.)	$n', n''$	$O - C$	$O - C$
5597.85 (8)	17859.1	$\beta(0, 0) R$	- 0.1	
5603.81 (3)	17840.1	$\beta(0, 0) Q$	- 0.1	
5629.28 (7)	17759.3	$\beta(1, 1) R$	+ 0.3	
5635.27 (2)	17740.4	$\beta(1, 1) Q$	+ 0.3	
5661.55 (7)	17658.1	$\beta(2, 2) R$	- 0.2	
5667.59 (2)	17639.3	$\beta(2, 2) Q$	- 0.2	
5694.42 (4)	17556.2	$\beta(3, 3) R$	- 0.7	
5700.61 (2)	17537.1	$\beta(3, 3) Q$	- 1.3	
5727.43 (3)	17455.0	$\beta(4, 4) R$	0.0	
5733.40 (2)	17436.8	$\beta(4, 4) Q$	0.0	
5759.56 (4)	17357.6	$\alpha(0, 2) R_b$	- 0.7	
5761.99 (6)	17350.3	$\alpha(0, 2) R_c$	+ 0.8	
5811.16 (5)	17203.5	$\alpha(1, 3) R_b$	- 2.6	
5814.96 (6)	17192.2			
5863.01 (4)	17051.3	$\{ \alpha(2, 4) R_b$ $\gamma(7, 3) R_a$	- 2.5 + 1.5	+ 0.3
5870.56 (2)	17029.4			
5872.71 (2)	17023.2			
5904.86 (5)	16930.5			
5922.02 (5)	16881.5			
5926.06 (3)	16870.0			
5949.92 (3)	16802.3			
5954.64 (2)	16789.0			
5961.27 (1)	16770.3			
6006.48 (3)	16645.0			
6034.66 (1)	16566.4			
6051.02 (3)	16521.6			
6057.59 (2)	16503.6			
6064.70 (2)	16484.3	$\gamma(4, 1) Q_b$		
6148.79 (2)	16258.9	$\gamma(5, 2) R_c$	+ 0.8	+ 1.8
6159.26 (2)	16231.3	$\alpha(1, 4) R_b$	- 2.8	
6162.23 (2)	16223.4			
6174.55 (3)	16191.0			
6183.45 (2)	16167.7			
6186.64 (5)	16159.4			
6190.09 (3)	16150.4			
6215.24 (6)	16085.0	$\gamma(6, 3) Q_c$		
6222.37 (4)	16066.0			
6226.31 (3)	16056.4			
6268.31 (3)	15948.9	$\alpha(3, 6) R_a$	- 0.5	
6275.44 (1)	15930.2	$\gamma(8, 5) R_a$	+ 2.1	+ 6.6
6321.66 (1)	15814.7	$\gamma(2, 0) R_b$	+ 0.3	+ 0.4
6334.82 (1)	15781.6			
6350.44 (1)	15743.1	$\gamma(2, 0) R_c$	+ 1.7	+ 3.4
6354.72 (1)	15732.6	$\gamma(2, 0) Q_c$		
6371.29 (1)	15691.9			
6382.91 (1)	15658.9	$\gamma(3, 1) R_b$	+ 0.2	+ 0.9
6399.56 (1)	15621.5	$\gamma(9, 6) R_c$	+ 1.6	- 6.2
6414.19 (1)	15586.3	$\gamma(3, 1) R_c$	+ 1.1	+ 2.9
6447.78 (1)	15505.4	$\gamma(4, 2) R_b$	+ 0.9	+ 1.8
6479.02 (1)	15430.2	$\gamma(4, 2) R_c$	- 0.1	+ 1.2
6483.64 (2)	15419.2	$\gamma(4, 2) Q_c$		
6510.84 (1)	15354.8			
6512.60 (1)	15350.6	$\gamma(5, 3) R_b$	- 1.1	- 0.6
6517.29 (1)	15339.6	$\gamma(5, 3) Q_b$		
6543.78 (1)	15276.6	$\gamma(5, 3) R_c$	- 0.1	0.0
6551.44 (1)	15264.0	$\alpha(1, 5) R_c$	+ 1.2	
6562.17 (1)	15234.7	$\alpha(8, 11) R_c$	+ 2.6	
6579.01 (1)	15195.7			
6594.01 (1)	15161.1			
6626.08 (2)	15087.7	$\alpha(9, 12) R_a$	- 1.3	
6634.30 (2)	15069.0			
6651.46 (5)	15030.1	$\gamma(1, 0) R_a$	+ 1.5	+ 0.1
6657.73 (2)	15016.0	$\gamma(1, 0) Q_a$		
6681.06 (6)	14963.6	$\gamma(1, 0) R_b$	+ 0.3	+ 0.3
6685.97 (1)	14952.7	$\gamma(1, 0) Q_b$		
6691.21 (4)	14940.9	$\alpha(10, 13) R_b$	- 1.7	
6714.37 (6)	14889.4	$\gamma(1, 0) R_c$	- 0.3	+ 0.7

$\lambda$ (air)	$\nu$ (vac.)	$n', n''$	$O - C$	$O - C$
6719.32 (6)	14878.6	$\gamma(1, 0) Q_c$	- 0.3	- 2.8
6723.95 (5)	14868.2	$\gamma(2, 1) R_a$		
6747.80 (5)	14815.6	$\gamma(2, 1) Q_a$	+ 0.3	+ 0.9
6751.81 (4)	14806.8	$\gamma(2, 1) Q_b$		
6756.30 (6)	14797.0	$\alpha(11, 14) R_b$	- 2.1	
6781.93 (5)	14741.3	$\gamma(2, 1) R_c$	- 0.2	+ 0.9
6785.81 (4)	14732.6	$\gamma(2, 1) Q_c$		
6815.27 (5)	14669.1	$\gamma(3, 2) R_a$	+ 0.4	+ 2.1
6820.17 (3)	14658.5	$\gamma(3, 2) R_b$	+ 0.4	+ 1.1
6850.23 (5)	14594.0	$\gamma(3, 2) Q_b$		
6852.33 (6)	14588.0	$\gamma(3, 2) R_c$	- 0.6	+ 0.6
6858.06 (4)	14577.5	$\gamma(4, 3) R_a$	- 0.2	+ 1.8
6883.84 (3)	14522.8	$\gamma(4, 3) Q_a$		
6919.55 (4)	14447.9	$\gamma(4, 3) R_b$	- 0.8	+ 0.3
6925.76 (2)	14435.0	$\gamma(4, 3) R_c$	- 1.1	- 0.6
6941.89 (1)	14401.4	$\gamma(5, 4) R_a$	+ 0.7	+ 1.1
6988.51 (1)	14305.3	$\gamma(5, 4) Q_a$		
7054.51 (8)	14171.4	$\gamma(5, 4) R_c$	+ 0.6	- 0.2
7060.01 (3)	14160.4	$\gamma(0, 0) R_a$	0.0	0.0
7087.89 (12)	14104.7	$\gamma(0, 0) Q_a$		
7093.17 (4)	14094.0	$\gamma(0, 0) R_b$	0.0	0.0
7125.61 (14)	14030.1	$\gamma(0, 0) Q_b$		
7131.34 (5)	14018.7	$\gamma(0, 0) R_c$	+ 1.1	- 0.3
7159.03 (6)	13964.5	$\gamma(1, 1) R_a$		
7164.31 (4)	13954.2	$\gamma(0, 0) Q_c$		
7171.22 (5)	13940.8	$\gamma(1, 1) Q_a$		
7183.00 (10)	13917.9	$\gamma(1, 1) R_b$	+ 0.2	+ 0.8
7197.67 (8)	13889.6	$\gamma(1, 1) Q_b$		
7203.64 (4)	13878.1	$\alpha(4, 9) R_b$	- 0.8	
7219.40 (6)	13847.8	$\gamma(1, 1) R_c$		
7230.44 (4)	13825.1	$\gamma(2, 2) R_a$	- 0.2	+ 0.5
7269.05 (6)	13752.6	$\gamma(2, 2) Q_a$	+ 1.7	+ 2.6
7273.93 (5)	13743.9	$\gamma(3, 3) R_b$	- 0.4	- 1.5
7290.80 (5)	13712.1	$\gamma(2, 2) R_c$		
7297.01 (3)	13700.4	$\gamma(2, 2) Q_b$		
7303.04 (5)	13689.1	$\gamma(1, 1) Q_c$		
7589.62 (8)	13172.3	$\gamma(2, 2) R_b$	- 0.2	+ 0.5
7596.03 (3)	13161.1	$\gamma(2, 2) Q_b$	+ 1.7	+ 2.6
7628.13 (8)	13105.8	$\gamma(3, 3) R_a$	- 0.4	- 1.5
7634.08 (4)	13095.6	$\gamma(2, 2) Q_c$		
7666.43 (6)	13040.3	$\gamma(3, 3) Q_a$		
7672.10 (10)	13030.7	$\gamma(3, 3) R_b$	+ 1.3	+ 1.7
7679.33 (4)	13018.4	$\gamma(0, 1) R_a$	+ 0.5	+ 0.5
7705.21 (8)	12974.7	$\gamma(0, 1) Q_a$		
7713.40 (4)	12960.9	$\gamma(0, 1) R_b$	+ 0.2	+ 0.7
7743.24 (4)	12910.9	$\gamma(0, 1) Q_b$		
7749.76 (4)	12900.1	$\gamma(0, 1) R_c$	+ 0.6	- 0.1
7755.82 (4)	12890.0	$\gamma(1, 2) R_a$	+ 0.5	+ 0.2
7783.44 (2)	12844.3	$\gamma(0, 1) Q_c$		
7820.11 (8)	12784.0	$\gamma(1, 2) R_b$	+ 0.4	+ 1.0
7828.04 (10)	12771.1	$\gamma(1, 2) Q_b$		
7861.00 (6)	12717.5	$\gamma(1, 2) R_c$	+ 0.4	+ 0.1
7900.92 (4)	12653.3	$\gamma(2, 3) R_a$	+ 0.9	+ 1.0
7907.33 (6)	12643.0	$\gamma(1, 2) Q_a$		
7948.60 (8)	12577.4	$\gamma(2, 3) Q_a$		
7988.05 (4)	12515.3	$\gamma(1, 2) Q_c$	- 0.1	+ 0.2
		$\gamma(2, 3) R_b$	- 0.2	+ 0.9
		$\gamma(3, 4) R_a$	+ 1.5	+ 1.6
		$\gamma(2, 3) Q_b$		
		$\gamma(3, 4) R_b$	+ 1.5	+ 1.1
		$\gamma(3, 4) Q_b$	- 7.5	- 4.0
		$\gamma(4, 5) R_a$ (?)	+ 1.8	+ 1.2
		$\gamma(4, 5) R_c$		
		$\gamma(4, 5) Q_a$		
		$\gamma(4, 5) Q_b$		
		$\gamma(4, 5) R_b$		
		$\gamma(4, 5) Q_c$		
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		$\gamma(4, 5) R_a$		
		$\gamma(4, 5) Q_c$		
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		$\gamma(4, 5) Q_c$		
		$\gamma(4, 5) R_b$		



There is no conclusive evidence for a term in  $(n' + \frac{1}{2})(n'' + \frac{1}{2})$ , the coefficient of which is usually small, and may here be indeterminable on account of uncertainty in the exact position of the heads; the absence of this term would indicate that the  $R$  head is near the origin. Table 4 is too incomplete and the data insufficiently accurate for the determination of vibrational constants from the  $Q$  heads; these limitations are due to the facts that these fainter heads become lost in the overlapping sequences, and that the heads are not sufficiently well defined for accurate measurement.

Table 2.  $R$  and  $Q$  heads of the orange system  $\beta$ 

$n''$		0	1	2	3	4
$n'$						
0	$R$	17859.1				
	$Q$	17840.1				
	$\Delta R$		99.8			
	$\Delta Q$		99.7			
1	$R$		17759.3			
	$Q$		17740.4			
	$\Delta R$			101.2		
	$\Delta Q$			101.1		
2	$R$			17658.1		
	$Q$			17639.3		
	$\Delta R$				101.9	
	$\Delta Q$				102.2	
3	$R$				17556.2	
	$Q$				17537.1	
	$\Delta R$					101.2
	$\Delta Q$					100.3
4	$R$					17455.0
	$Q$					17436.8

## § 5. ANALYSIS OF STRUCTURE

The equations for the triplet sequences of the heads in Table 3, in the form obtained by means of the new quantum mechanics, are:

$$\left. \begin{aligned} \nu &= 14243.7 + \{864.60(n' + \tfrac{1}{2}) - 3.675(n' + \tfrac{1}{2})^2\} \\ &\quad - \{1009.85(n'' + \tfrac{1}{2}) - 5.125(n'' + \tfrac{1}{2})^2\} \quad \dots\dots(a) \\ \nu &= 14175.5 + \{866.27(n' + \tfrac{1}{2}) - 3.81(n' + \tfrac{1}{2})^2\} \\ &\quad - \{1008.15(n'' + \tfrac{1}{2}) - 4.54(n'' + \tfrac{1}{2})^2\} \quad \dots(2)\dots(b) \\ \nu &= 14100.7 + \{867.57(n' + \tfrac{1}{2}) - 3.98(n' + \tfrac{1}{2})^2\} \\ &\quad - \{1009.15(n'' + \tfrac{1}{2}) - 4.64(n'' + \tfrac{1}{2})^2\} \quad \dots\dots(c). \end{aligned} \right\}$$

According to these equations the separations of the triplets, expressed in wave-numbers, depend on  $n$ , but Tables 3 and 4 seem to indicate accidental rather than real variations in them; this discrepancy may be due to the fact that the measurements were made on the heads. If the separations are constant, the coefficients of  $(n + \frac{1}{2})$  and  $(n + \frac{1}{2})^2$  would be the same for  $R_a$ ,  $R_b$  and  $R_c$ , and then the wave-numbers of the heads would be given by equation (3):

$$\nu = \left\{ \begin{array}{l} 14242.6 \\ 14175.9 \\ 14101.3 \end{array} \right\} + \{866.24(n' + \tfrac{1}{2}) - 3.82(n' + \tfrac{1}{2})^2\} - \{1009.07(n'' + \tfrac{1}{2}) - 4.75(n'' + \tfrac{1}{2})^2\} \quad \dots\dots(3),$$

where the coefficients are obtained from averages of  $\Delta a$ ,  $\Delta b$  and  $\Delta c$  in a given triple row or column of Table 3. Since the evidence for constant separation is inde-

cisive, wave-numbers have been calculated from equations (2) and (3), and the differences between these and those observed are shown in columns (4) and (5) of Table 3.

For the sake of comparison with Birge and Christy's equation\* for the blue-green system  $\alpha$ , their equation is converted from the form of the older quantum theory to the form used above and becomes:

$$\begin{aligned} (a) \quad & \left\{ \begin{array}{l} 19434.48 \\ 19432.58 \\ 19423.75 \end{array} \right\} + \{837.86 (n' + \tfrac{1}{2}) - 4.546 (n' + \tfrac{1}{2})^2\} \\ (b) \quad \nu = & \quad \quad \quad - \{1008.12 (n'' + \tfrac{1}{2}) - 4.519 (n'' + \tfrac{1}{2})^2\}. \\ (c) \end{aligned}$$

It is obvious that since the coefficients of  $(n'' + \frac{1}{2})$  and  $(n'' + \frac{1}{2})^2$  are the same in equation (2) as in Birge and Christy's equation, the final energy level in system  $\gamma$ , exhibited in Table 3, is the same as that of system  $\alpha$ , analysed by those authors. In the latter the evidence obtained by them for the character of the electronic transition is most in favour of  ${}^3\Pi \rightarrow {}^3\Pi$ . They regarded the final state as the lowest excited  ${}^3\Pi$  state of the TiO molecule, and by analogy with CO they suggested that the normal state is of the  ${}^1\Sigma$  type.

It was suggested to the author by Mr R. W. B. Pearse that the molecule TiO with thirty electrons might resemble in electronic configuration the atom Ca with ten fewer electrons, and that the character of the electronic transitions responsible for the new systems  $\beta$  and  $\gamma$  might be found by comparison with the transitions responsible for the more prominent singlets and triplets of Ca.

The resemblance in electronic configuration between a molecule and an atom of ten fewer electrons implies, according to Pearse, that each constituent of the molecule not only retains its own two K electrons but also has a complete ring of eight L electrons. If this is true, then for the molecule TiO, O, having gained two electrons from Ti, resembles as a constituent of the molecule inactive Ne, while Ti having lost two electrons resembles Ca; herein lies a feasible explanation of the resemblance in transitions of Ca and TiO.

In Ca the normal ("ground") state is  $4\,{}^1S$  and the lowest four excited states are  $4\,{}^3P$ ,  $4\,{}^1P$ ,  $4\,{}^3S$  and  $5\,{}^3P$  as shown in Fig. 1 (a), the well-known flame line  $\lambda\,4226.73$ ,  $\nu\,23652.4$  being due to  $4\,{}^1P \rightarrow 4\,{}^1S$ † and the orange triplet  $\lambda\lambda\,6102.72$ ,  $6122.22$ ,  $6162.18$ ,  $\nu\nu\,16381.7$ ,  $16329.5$ ,  $16223.6$  to the transition  $4\,{}^3S \rightarrow 4\,{}^3P$ . The transition  $5\,{}^3P \rightarrow 4\,{}^3P$  is, of course, not represented in the atomic spectrum by an observed triplet, but the wave-number corresponding to it may be obtained from the known values of the Ca terms; since the ratio of wave-numbers of the various analogous electronic transitions in atoms and molecules is only roughly the same, and since the transitions involve such numbers as 20000, it is immaterial which members of the  ${}^3P$  terms are used. Thus, taking the middle terms, we obtain:

$$5\,{}^3P_1 \rightarrow 4\,{}^3P_1 = 34094.6 - 12750.2 = 21344.4.$$

Comparing this number with  $\nu_e$  obtained by Birge and Christy, we get for the Ca/TiO ratio:

$$\frac{21344.4}{19432.6} = 1.1.$$

\* By private communication, also *Phys. Rev.* 33, 701 (1929).

† Fowler, *Report*, p. 122-4.

Table 3. R heads of bands in red-infra-red system  $\gamma$

$n''$	$\circ$	$\Delta''a$ $\Delta''b$ $\Delta''c$	I	2	3	4	5
$n'$							
$\circ$	$\begin{Bmatrix} a \\ b \\ c \end{Bmatrix}$	$\begin{Bmatrix} 999.1 \\ 998.9 \\ 999.5 \end{Bmatrix}$	$\begin{Bmatrix} 13172.3 \\ 13105.8 \\ 13030.6 \end{Bmatrix}$	$\begin{Bmatrix} 66.5 \\ 75.2 \\ 837.8 \end{Bmatrix}$			
	$\begin{Bmatrix} \Delta'a \\ \Delta'b \\ \Delta'c \end{Bmatrix}$	$\begin{Bmatrix} 858.7 \\ 858.9 \\ 859.3 \end{Bmatrix}$	$\begin{Bmatrix} 858.2 \\ 858.2 \\ 858.2 \end{Bmatrix}$				
I	$\begin{Bmatrix} a \\ b \\ c \end{Bmatrix}$	$\begin{Bmatrix} 1000.0 \\ 999.1 \\ 999.6 \end{Bmatrix}$	$\begin{Bmatrix} 14030.1 \\ 13064.5 \\ 13889.8 \end{Bmatrix}$	$\begin{Bmatrix} 989.8 \\ 989.8 \\ 989.7 \end{Bmatrix}$	$\begin{Bmatrix} 13040.3 \\ 12974.7 \\ 12900.1 \end{Bmatrix}$	$\begin{Bmatrix} 65.6 \\ 74.6 \\ 849.3 \end{Bmatrix}$	
	$\begin{Bmatrix} \Delta'a \\ \Delta'b \\ \Delta'c \end{Bmatrix}$	$\begin{Bmatrix} 851.1 \\ 851.1 \\ 851.1 \end{Bmatrix}$	$\begin{Bmatrix} 848.5 \\ 848.5 \\ 848.5 \end{Bmatrix}$				
2	$\begin{Bmatrix} a \\ b \\ c \end{Bmatrix}$	$\begin{Bmatrix} 999.1 \\ 1001.6 \end{Bmatrix}$	$\begin{Bmatrix} 14878.6 \\ 14815.6 \\ 14741.3 \end{Bmatrix}$	$\begin{Bmatrix} 989.0 \\ 990.5 \\ 988.7 \end{Bmatrix}$	$\begin{Bmatrix} 978.7 \\ 980.8 \\ 981.5 \end{Bmatrix}$	$\begin{Bmatrix} 12910.9 \\ 12844.3 \\ 12771.1 \end{Bmatrix}$	$\begin{Bmatrix} 60.6 \\ 73.2 \\ 84.7 \end{Bmatrix}$
	$\begin{Bmatrix} \Delta'a \\ \Delta'b \\ \Delta'c \end{Bmatrix}$	$\begin{Bmatrix} 843.3 \\ 843.3 \\ 843.3 \end{Bmatrix}$	$\begin{Bmatrix} 841.4 \\ 841.4 \\ 841.4 \end{Bmatrix}$				
3	$\begin{Bmatrix} a \\ b \\ c \end{Bmatrix}$	$\begin{Bmatrix} 999.1 \\ 1001.6 \end{Bmatrix}$	$\begin{Bmatrix} 15658.9 \\ 15586.3 \end{Bmatrix}$	$\begin{Bmatrix} 989.8 \\ 992.3 \end{Bmatrix}$	$\begin{Bmatrix} 980.0 \\ 980.0 \end{Bmatrix}$	$\begin{Bmatrix} 13752.6 \\ 13689.1 \end{Bmatrix}$	$\begin{Bmatrix} 968.6 \\ 971.6 \end{Bmatrix}$
	$\begin{Bmatrix} \Delta'a \\ \Delta'b \\ \Delta'c \end{Bmatrix}$	$\begin{Bmatrix} 836.0 \\ 836.0 \end{Bmatrix}$	$\begin{Bmatrix} 836.0 \\ 836.0 \end{Bmatrix}$				
4	$\begin{Bmatrix} a \\ b \\ c \end{Bmatrix}$			$\begin{Bmatrix} 15505.4 \\ 15430.2 \end{Bmatrix}$	$\begin{Bmatrix} 982.6 \\ 982.3 \end{Bmatrix}$	$\begin{Bmatrix} 14588.0 \\ 14522.8 \end{Bmatrix}$	$\begin{Bmatrix} 66.5 \\ 74.5 \end{Bmatrix}$
	$\begin{Bmatrix} \Delta'a \\ \Delta'b \\ \Delta'c \end{Bmatrix}$			$\begin{Bmatrix} 827.8 \\ 827.8 \end{Bmatrix}$			
5	$\begin{Bmatrix} a \\ b \\ c \end{Bmatrix}$			$\begin{Bmatrix} 16258.9 \end{Bmatrix}$	$\begin{Bmatrix} 982.3 \end{Bmatrix}$	$\begin{Bmatrix} 15350.6 \\ 15276.6 \end{Bmatrix}$	$\begin{Bmatrix} 14447.9 \\ 14305.3 \end{Bmatrix}$
7	$\begin{Bmatrix} a \end{Bmatrix}$					$\begin{Bmatrix} 17051.3 \end{Bmatrix}$	$\begin{Bmatrix} 12653.3 \\ 12515.3 \end{Bmatrix}$

Table 4. Q heads of bands in red-infra-red system  $\gamma$ 

$n'$		0	$\Delta'a$ $\Delta'b$ $\Delta'c$	I	$\Delta'a$ $\Delta'b$ $\Delta'c$	2	$\Delta'a$ $\Delta'b$ $\Delta'c$	3	$\Delta'a$ $\Delta'b$ $\Delta'c$	4	5
$n'$											
0	$a$ $b$ $c$	$\left\{ \begin{array}{l} 14160.4 \\ 14094.0 \\ 14018.7 \end{array} \right\}$ 835.6 858.7 861.0	$\left\{ \begin{array}{l} 999.3 \\ 998.4 \\ 1000.3 \end{array} \right\}$	$\left\{ \begin{array}{l} 13161.1 \\ 13095.6 \\ 13018.4 \end{array} \right\}$ 837.6 858.6 859.7							
I	$a$ $b$ $c$	$\left\{ \begin{array}{l} 15016.0 \\ 14952.7 \\ 14878.6 \end{array} \right\}$ ..... .....	$\left\{ \begin{array}{l} 997.3 \\ 998.5 \\ 1000.5 \end{array} \right\}$	$\left\{ \begin{array}{l} 14018.7 \\ 13954.2 \\ 13878.1 \end{array} \right\}$ 849.5 852.6 854.5	$\left\{ \begin{array}{l} 988.1 \\ 993.3 \\ 988.1 \end{array} \right\}$	$\left\{ \begin{array}{l} 13030.6 \\ 12960.9 \\ 12890.0 \end{array} \right\}$ 69.7 70.9 847.6					
2	$a$ $b$ $c$	$\left\{ \begin{array}{l} 15732.6 \\ \dots \dots \dots \end{array} \right\}$	$\left\{ \begin{array}{l} 1000.0 \end{array} \right\}$	$\left\{ \begin{array}{l} 14868.2 \\ 14806.8 \\ 14732.6 \end{array} \right\}$ 61.4 74.2 988.7	$\left\{ \begin{array}{l} 990.0 \\ \dots \dots \dots \end{array} \right\}$	$\left\{ \begin{array}{l} 13878.2 \\ \dots \dots \dots \end{array} \right\}$ 978.1	$\left\{ \begin{array}{l} 12900.1 \end{array} \right\}$				
3	$a$ $b$ $c$								$\left\{ \begin{array}{l} 972.8 \\ \dots \dots \dots \end{array} \right\}$	$\left\{ \begin{array}{l} 12771.1 \\ \dots \dots \dots \end{array} \right\}$	
4	$a$ $b$ $c$										$\left\{ \begin{array}{l} 12643.0 \\ 12577.4 \\ 12502.8 \end{array} \right\}$ 65.6 74.6
5	$a$ $b$ $c$									$\left\{ \begin{array}{l} 14435.0 \\ \dots \dots \dots \end{array} \right\}$	
6	$a$ $b$ $c$										$\left\{ \begin{array}{l} 16085.0 \\ \dots \dots \dots \end{array} \right\}$

Now for the infra-red system  $\gamma$ , Equation (2), the  $\nu_0$  values of the origin are about 14233, 14165, 14090, and the Ca lines comparable with these will be expected to lie in the neighbourhood of  $\nu\nu$  15656, 15582, 15499 (obtained by multiplying the TiO values by 1.1); these are not far from the orange Ca triplet  $4^3S \rightarrow 4^3P$ , mentioned above.

Again for the orange system  $\beta$  the (0, 0) band head is at  $\nu$  17859 and  $\nu_0$  is not far removed therefrom, say  $\nu_0 \doteq 17840 + 100/2 = 17890$ ; the corresponding Ca line would be expected in the neighbourhood of  $17890 \times 1.1 = 19679$ . The nearest strong Ca line to this is the flame line  $4^1P \rightarrow 4^1S$ ,  $\nu$  23652.4.

We may then tentatively assign to system  $\gamma$  a transition  $^3\Sigma \rightarrow ^3\Pi$ , the final  $^3\Pi$  state being also that of the blue-green system  $\alpha$ ; likewise we may assign to system  $\beta$  a transition  $^1\Pi \rightarrow ^1\Sigma$ , the final  $^1\Sigma$  state being the normal state of the TiO molecule, as was conjectured by Birge and Christy. These interpretations are in accordance with the facts (1) that both the systems  $\beta$  and  $\gamma$  have strong  $Q$  branches, as we should expect from a transition  $\Pi \rightleftharpoons \Sigma$ , and (2) that each band of system  $\gamma$  has three  $R$  and three  $Q$  heads, while each band of system  $\beta$  has only one  $R$  and one  $Q$  head.

Accepting these electronic transitions for systems  $\beta$  and  $\gamma$ , we are still unable to construct an energy level diagram for TiO, for lack of a system which could be attributed to a transition between one of the triplet states and one of the singlet states. In order to make a possible representation of the TiO energy levels, we must further invoke the Ca/TiO ratios used above. Now in Ca the difference  $4^1S - 4^3P$  works out to be  $\nu\nu$  15316, 15210, 15158. We may for the present take ten-elevenths of these values to represent the corresponding differences  $^3\Pi \rightarrow ^1\Sigma$  in TiO, and thus roughly locate the lowest excited state  $^3\Pi$  with respect to the normal state  $^1\Sigma$ . This is the basis on which Fig. 1 (b) has been constructed. With one exception the triplet separations in both Figs. 1 (a) and 1 (b) have been magnified about ten times; that exception is in the case of the vertical lines representing the triplet in the  $\alpha$  system of TiO, the separations between which have been magnified about a hundred times.

Finally we may conclude that the  $\Delta\nu$  separation of the triplets, namely,  $Q_a - Q_b = 66$  and  $Q_b - Q_c = 75$  cm.<sup>-1</sup>, found for system  $\gamma$ , pertains to the  $^3\Pi$  level and therefore also to the final level of the blue-green system  $\alpha$ . Combining these final  $^3\Pi$  separations with Birge and Christy's  $\Delta\nu_R$  differences for system  $\alpha$ , namely,  $R_a - R_b = 1.9$ ,  $R_b - R_c = 8.8$ , we find for the initial  $^3\Pi$  state the approximate separations  $\Delta^3\Pi = 64$  and 66 cm.<sup>-1</sup>.

## § 6. ACKNOWLEDGMENTS

The author thanks most appreciatively Prof. A. Fowler for his valuable suggestions, guidance and criticisms during the execution of this work; also Dr W. Jevons and Mr R. W. B. Pearse for their kind criticisms and help in the analysis of the gross structure of the bands of system  $\gamma$ .

## § 7. DESCRIPTION OF PLATE

*Spectrograms of TiO bands from  $\lambda$  5600– $\lambda$  8800.*

- (a) From panchromatic plate, exposure 22 seconds, showing the 0 sequence of the orange system  $\beta$  and some bands not treated in this paper.  
 (b) From panchromatic plate, exposure 22 seconds, showing (2, 0) band of system  $\gamma$  and some bands not treated in this paper.  
 (c) From panchromatic plate, exposure 30 seconds, showing three bands of the  $-2$  sequence, three of the  $-1$  sequence, and a few not treated in this paper.  
 (d) and (e) From kryptocyanine plates, exposure 16 and 9 minutes respectively; both show the  $-1$ , 0 and part of the  $+1$  sequences of system  $\gamma$ .  
 (f) From neocyanine plate, exposure 90 minutes, showing the 0 and  $+1$  sequences of system  $\gamma$ .

The wave-length scale is only approximate.

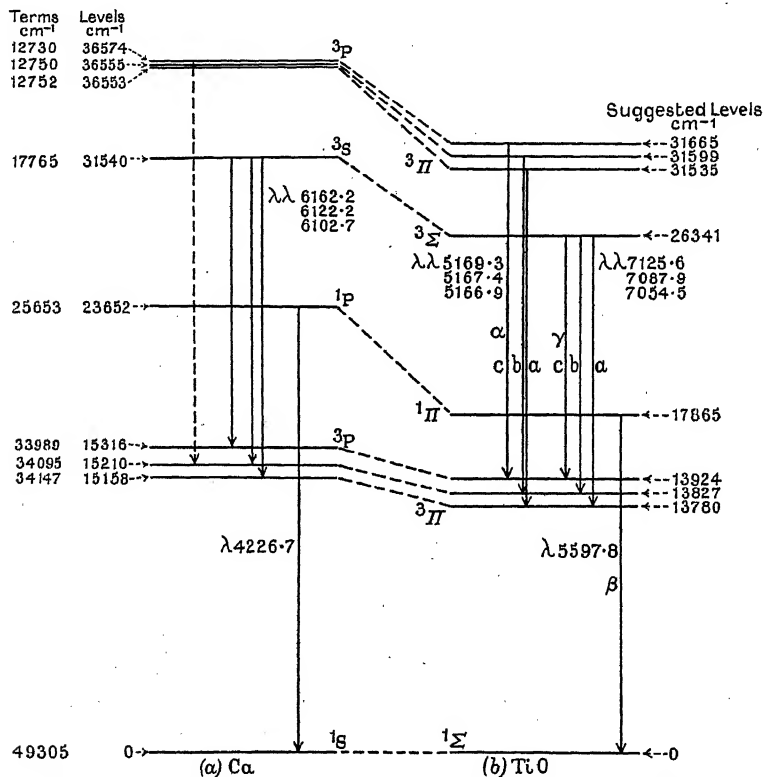


Fig. 1. Comparison of electronic energy transitions in Ca and TiO.

## DISCUSSION

Dr W. JEVONS: I congratulate the author on showing the connection between the two new systems  $\beta$  and  $\gamma$  and the previously known system  $\alpha$ , on the "rotational" analysis of which she had already spent much time and thought when Birge and Christy's successful result was first announced. It should be pointed out that Miss Lowater announced the discovery and interpretations of both systems  $\beta$

and  $\gamma$  in *Nature*, April 27, and that since the completion of her present paper Christy has arrived at a similar result for  $\gamma$  only (*Nature*, June 8).

In 1924 I analysed the  ${}^1\Pi \rightarrow {}^1\Sigma$  system of SiO, corresponding to the "4th positive" system of CO; it now appears that the analogous system of TiO (the monoxide of the next atom of column 4 of the periodic table) is Miss Lowater's system  $\beta$ , and it is interesting to note that although in CO and in SiO this transition is represented by a rather extensive system in the ultraviolet, in TiO it gives only a one-sequence system in the orange region. As CO gives about nine known systems and TiO three, one would expect SiO to have more than one system already analysed and the few unassigned bands recorded by Cameron\*, and it would be well if Miss Lowater could include in her work on these oxides an examination of SiO in the red and infra-red regions.

The occurrence in the galley proof, § 2, of the notation TiI for the spectrum of the neutral atom Ti, reminds me that many workers share my own opinion that this notation MI, MII, MIII, ..., first used by the late Sir Norman Lockyer, for what we now know to be the spectra of the atom and its ions, should be abandoned in favour of the more definite and informative notation M,  $M^+$ ,  $M^{++}$ , .... As usually printed MI looks more like an iodide than an atom. I personally have to pause a little to recall the fact that the degree of ionisation is one less than the affixed Roman numeral.

MR C. V. JACKSON: I thoroughly agree with Dr Jevons' suggestion, but I regard the new notation as a sad consequence of the sometimes excessive lack of conservatism of spectroscopists. For cases such as Millikan's "stripped atoms," e.g. SVI, it is perhaps easier to put the Roman numeral notation than to write  $S^{++++}$ . But for cases of singly or doubly ionised atoms the  $M^+$  notation is more expressive and eliminates the irritating mental arithmetic needed for the other notation. But perhaps the case is somewhat similar to that of the notation used for spectral terms. Before terms of higher multiplicity, then triplet, were discovered the beautiful notation of Fowler, viz. Capital, Greek and Italic letters for singlet, doublet and triplet terms respectively, was perfect, but when the higher multiplicities were found it was necessary to use the new notation, and for the sake of uniformity the singlet, doublet and triplet terms had to be expressed in it too. But the justification for the change from the  $M^+$  notation for ionised atoms is not nearly so great as that for the change in the spectral term notation. However, it is gratifying to note that the  $M^+$  notation has been used in the revision of Rowland's *Solar Wavelength Tables* (1928). The "stripped atom" of Cl, for instance, would, I submit, be denoted better by  $Cl^{6+}$  than by the usual CIVII.

DR W. JEVONS: The difficulty mentioned by Mr Jackson can be met by the use of index numerals.

AUTHOR'S reply: I thank Dr Jevons for his criticism and kind remarks. With regard to the symbol TiI, I took it direct from Russell's paper in the *Astrophysical Journal*, regarding this as authoritative.

\* *Phil. Mag.* 3, 110 (1925).

# NOTES ON SOME RADIATION HEAT TRANSFER FORMULAE

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**ABSTRACT.** The general expression for the radiation heat transfer from a surface is first considered, after which some simple cases are examined, i.e., parallel planes, concentric spheres, etc. Some general conclusions are then drawn for the case of a surface completely surrounded by other surfaces at a uniform temperature, but of no particular simple shape; it is pointed out that whatever the shapes, sizes, and relative positions of the various surfaces, the heat transfer per unit area must always lie between minimum and maximum values depending only upon temperatures and emissivities.

Lastly, an approximate formula is given for the heat transfer when the surroundings are poor reflectors; this is applied to two non-concentric spheres, one within the other.

## § 1. INTRODUCTION

THE following notes contain some simple results dealing principally with the effects of reflected radiation upon the transfer of heat between a surface and its surroundings. The ground covered is to some extent semi-familiar, partly through the medium of analogous problems in optics, but so far as the author is aware the majority of the conclusions have not previously been pointed out.

## § 2. GENERAL FORMULA

The net rate of heat transfer by radiation from a surface at a known temperature  $T^\circ$  C. absolute in the presence of other surfaces at any maintained temperatures, is given by

$$H = \sigma e (1 - K) (T^4 - T_0^4) \text{ cal. per sq. cm. per sec.} \quad \dots\dots(1),$$

where  $e$  is the emissivity of the surface (assumed grey);

$\sigma$  Stefan's constant ( $1.36 \times 10^{-12}$  c.g.s. units);

$K$  the fraction of the radiation, emitted from the surface in question, which is returned to it by reflection from other surfaces and reabsorbed;

$T_0$  the equilibrium temperature (absolute) which the surface would tend to attain under the influence of radiation alone, if no heat were supplied to or withdrawn from it.

This result is easily proved. From the above definition of  $K$  it follows that the heat loss from the surface per unit area per second, taking into account only its own emission, is equal to  $\sigma e (1 - K) T^4$ . Since  $K$  is independent of the surface



temperature  $T$ , the corresponding heat loss at the equilibrium temperature  $T_0$  would be  $\sigma e (1 - K) T_0^4$ .

The heat gained by the given surface per unit area per second, owing to absorption of radiation emitted from other surfaces, does not depend upon the temperature of the given surface, and must therefore be equal to  $\sigma e (1 - K) T_0^4$  since in equilibrium the surface gains as much heat as it loses. Hence the expression for the heat loss from the surface when it is maintained at temperature  $T$  is given by the difference between  $\sigma e (1 - K) T^4$  and  $\sigma e (1 - K) T_0^4$ , i.e. by equation (1). The values of  $K$  and  $T_0$  depend in general upon the sizes, shapes, and relative positions of the various surfaces, as well as upon their temperatures and emissivities.

### § 3. SURFACE COMPLETELY SURROUNDED BY OTHER SURFACES AT A UNIFORM TEMPERATURE

In this case the equilibrium temperature  $T_0$  is, from the properties of a uniform temperature enclosure, equal to the uniform temperature  $T'$  of the surrounding surfaces. There remains the evaluation of  $K$ , which takes account of reflected radiation, and may be of considerable importance in some cases. It will be more convenient to consider one or two simple shapes of surfaces before coming to some general conclusions as to the limits within which  $K$  may vary.

### § 4. PARALLEL PLANE SURFACES

The radiation emitted from either surface undergoes reflection at each of the two surfaces alternately, and it is easily proved that

$K = e (1 - e') / (e + e' - ee')$  where  $e, e'$  are the emissivities of the two surfaces.

Equation (1) for the heat transfer per unit area per second from either surface therefore becomes

$$H = \frac{\sigma ee'}{e + e' - ee'} (T^4 - T'^4) \quad \dots\dots(2).$$

This particular result is well known, and is to be found in standard books on heat.

### § 5. CONCENTRIC SPHERES OR CYLINDERS

(a) *Internal surface of outer sphere (or cylinder) regularly reflecting.* From a brief consideration of the paths of the rays in these particular geometrical arrangements it will be seen that all the radiation emitted from the inner surface must, after suffering regular reflection at the outer surface, fall directly upon the inner surface again; this is true both for concentric spheres and concentric cylinders.

It makes no difference whether the inner sphere (or cylinder) is a regular or diffuse reflector; in either case the radiation reflected from it is incident upon it again after reflection at the outer surface, and so on. The radiation from the inner surface is therefore reflected at the outer and inner surfaces alternately, and the value of  $K$  is precisely the same as in the case of parallel plates already considered. The formula for the heat transfer is therefore the same as (2).

(b) *Internal surface of outer sphere (or cylinder) diffusely reflecting.* The radiation from the inner surface, after diffuse reflection at the outer surface, does not all fall again directly upon the inner surface, but some of it strikes other parts of the outer surface. Suppose  $\rho$  to represent the fraction of the diffusely reflected radiation which strikes the inner surface directly: the fraction  $(1 - \rho)$  undergoes another diffuse reflection at the outer surface, after which a fraction  $\rho$  of it is incident directly upon the inner surface, and so on. The total fraction of the emission from the inner surface which is again incident upon that surface after the series of outer-surface reflections is by addition equal to

$$\rho(1 - e') + \rho(1 - \rho)(1 - e')^2 + \dots = \rho(1 - e')/(\rho + e' - \rho e') = q, \text{ say.}$$

Part of the radiation thus returned to the inner surface is reflected from it and undergoes a series of outer-surface reflections similar to those just described in the case of the original emission.

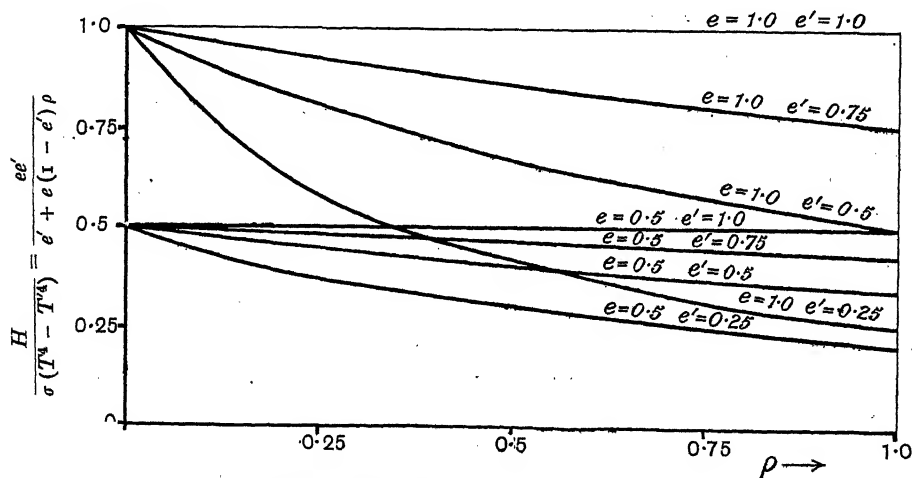


Fig. 1. Radiation between concentric cylinders or spheres.

Finally, these reflections are repeated indefinitely, and the fraction of the inner surface emission ultimately returning to it and undergoing reabsorption is given by

$$K = eq + eq^2(1 - e') + \dots = ep(1 - e')/(e' + pe - pee').$$

The expression for the net radiation heat transfer is therefore, from (1),

$$H = \frac{\sigma ee'}{e' + e(1 - e')\rho} (T^4 - T'^4) \quad \dots\dots(3).$$

This result is shown graphically in Fig. 1.

The value of  $\rho$  may be expressed in terms of the radii  $a$ ,  $b$ , of the inner and outer spheres (or cylinders) respectively. It is easily shown, from the usual cosine distribution law for diffuse reflection, that for concentric cylinders  $\rho = a/b$ , and for concentric spheres  $\rho = a^2/b^2$ . In either case  $\rho$  is equal to the ratio of corresponding areas of the inner and outer surfaces.

It will be noted that, as would be expected, expression (3) becomes identical with (2) as  $\rho \rightarrow 1$ .

Since completing the present notes the author has found that the result (3) is given by M. ten Bosch in his recent book *Die Wärmeübertragung*. The method of proof employed by M. ten Bosch is, however, considerably lengthier than the above, and no distinction is drawn between the cases of regular and diffuse reflectors.

#### § 6. SOME GENERAL CONCLUSIONS FOR THE CASE OF A SURFACE COMPLETELY SURROUNDED BY OTHERS AT A UNIFORM TEMPERATURE

It is important to determine generally the conditions under which the influence of reflected radiation (i.e.  $K$ ) may be of practical importance.

In the first place it will be noted that if  $e' = 1.0$ , i.e. if the surrounding surfaces are perfect absorbers,  $K = 0$  whatever the shapes, sizes and relative positions of the surfaces, and (1) becomes

$$H = \sigma e (T^4 - T'^4),$$

which is the usual simple formula employed in heat transfer calculations. This result is therefore strictly valid for "black" surroundings, from which of course no radiation is reflected.

If the surrounding surfaces are not perfect absorbers, the heat loss from the inner surface is less, to an extent depending upon  $K$ , equation (1), than it would be if they were black; obviously, the better the reflecting power of the surroundings (i.e. the smaller  $e'$ ), the greater  $K$  and the smaller the heat loss, other things being equal. But for surfaces of given emissivities  $K$  depends upon the shapes, sizes and relative positions of the inner and outer surfaces. Generally speaking the influence of reflected radiation is least ( $K$  least) when the inner surface has linear dimensions small in comparison with its surroundings, and is greatest when the inner and outer surfaces are of the same order of size, the conditions in the latter case closely approximating to those which hold in the case of parallel plates.

The influence of changes in the emissivity of the surrounding surfaces upon the heat transfer is least when the inner surface is relatively small;  $e'$  does not appear in the simple expression  $H = \sigma e (T^4 - T'^4)$ . It is greatest when the two surfaces are nearly the same size, for  $e$  and  $e'$  appear symmetrically in equation (2).

The case of two concentric cylinders or spheres, the outer one having a regularly reflecting internal surface, is exceptional in that the relative sizes make no difference to the heat transfer, but it may be pointed out that if the inner sphere or cylinder were small and slightly eccentrically placed, the heat loss would be considerably greater than when it is in the concentric position, since the geometrical conditions for the return of reflected radiation to the inner surface would no longer be fulfilled.

To sum up, it is interesting to note that, for given inner and outer surface emissivities  $e$  and  $e'$  respectively, the heat transfer must always lie between a maximum value given by  $H = \sigma e (T^4 - T'^4)$  and a minimum value given by

$H = \sigma e e' (T^4 - T'^4)/(e + e' - e e')$  whatever the shapes, sizes, relative positions, etc. of the surfaces. These two values may conveniently be read off from Fig. 1 in which they are represented by the ordinates corresponding to  $\rho = 0$  and  $\rho = 1$  respectively.

The maximum value corresponds to perfectly absorbing surroundings, and the minimum value to plane parallel surfaces. It will be seen from Fig. 1 that if the surroundings are not particularly good reflectors ( $e'$  not far from unity), these two expressions do not differ greatly. For instance, if  $e$  and  $e'$  are both equal to 0.50,  $H$  must lie between 0.50 and 0.33 times  $\sigma (T^4 - T'^4)$ ; and if  $e = e' = 0.75$ ,  $H$  lies between 0.75 and 0.60 times  $\sigma (T^4 - T'^4)$ .

With many ordinary surroundings  $e'$  would be about 0.90, and since in this case  $H$  cannot differ from the maximum value  $\sigma e (T^4 - T'^4)$  by more than 10 per cent. under any conditions, whatever the value of  $e$ , this simple formula cannot lead to very great error under such circumstances.

Nevertheless in some cases, as, for instance, with a calorimeter closely surrounded by an enveloping box, the reflected radiation may be by no means negligible. It is clear from the above considerations that, whereas coating the surface of a relatively small hot body with aluminium paint reduces the radiation heat transfer from the body to its surroundings in direct proportion to the change of surface emissivity, a similar treatment of the walls of the room in which the body is situated has no effect upon the heat loss.

On the other hand if the body were comparable in size with the room surrounding it, the heat loss, for given surface temperatures, would be reduced to practically the same extent by the coating of either the body or the surrounding walls with aluminium paint, assuming of course that both surfaces have the same emissivity before painting.

In the particular case of an ordinary vacuum flask with two silvered (regularly reflecting) concentric cylindrical surfaces, the conditions are the same as for parallel plates, as has been shown in § 5 (a), and the silver coatings on the inner and outer surfaces are equally effective in diminishing radiation heat loss.

#### § 7. APPROXIMATE EXPRESSION FOR $K$ WHEN THE DIFFUSE REFLECTING POWER OF THE SURROUNDING SURFACES IS SMALL. CASE OF TWO NON-CONCENTRIC SPHERES

If the surrounding surfaces are poor enough reflectors for radiation undergoing more than one reflection at them to be neglected,  $K$  may be expressed in terms of integrals taken over the inner and outer surfaces.

If  $dS$ ,  $dS'$  denote elementary areas of the inner and outer surfaces respectively, and  $\theta$ ,  $\theta'$  represent the angles made by the normals to these areas with the line of length  $r$  joining them, the amount of radiation falling every second upon  $dS'$  from those parts of the inner surface which are visible from  $dS'$  is given by

$$EdS' \int \frac{\cos \theta \cdot \cos \theta' dS}{\pi r^2} = \phi EdS', \text{ say} \quad \dots\dots(4),$$

where  $E$  represents the radiation emitted from the inner surface in all directions per unit area per second and the integral extends over the part of the inner surface facing  $dS'$ .

The part of this radiation which, after diffuse reflection at  $dS'$ , falls upon the inner surface is given by

$$(1 - e') \phi E dS' \int \frac{\cos \theta \cdot \cos \theta' dS}{\pi r^2}$$

where the integral is to be taken over the part of the inner surface facing  $dS'$ , and is therefore identical with  $\phi$  as defined in (4). Hence the radiation from the parts of the inner surface facing  $dS'$  which returns to the inner surface after reflection at  $dS'$  is given by

$$(1 - e') \phi^2 E dS'.$$

Finally, integrating for all elements of area of the outer surface, we find that the radiation from the whole of the inner surface which returns to it per second after reflection at the outer surface is equal to

$$E (1 - e') \int \phi^2 dS'.$$

Since the inner surface absorbs a fraction  $e$  of the radiation falling upon it, and the total emission from the whole of the inner surface is  $ES$ ,

$$K = \frac{e(1 - e')}{S} \int \phi^2 dS' \quad \dots\dots(5),$$

where  $S$  denotes the total inner surface area, and the integral extends over the entire outer surface. No other reflected radiation need be taken into account since it has been postulated that radiation which has undergone more than one reflection at the outer surface is of negligible intensity.

As an example, consider the particular case of two non-concentric spheres one within the other. The value of  $\phi$  at any point on the outer sphere at a distance  $x$  from the centre of the inner sphere is easily seen from (4) to be equal to

$$a^2 (b^2 + x^2 - c^2) / 2\pi b x^3,$$

where  $a$  and  $b$  are the radii of the inner and outer spheres and  $c$  is the distance apart of their centres ( $c < b - a$ ).

Hence from (5) the value of  $K$  is given by

$$\begin{aligned} K &= \frac{e(1 - e') a^2}{8bc} \int_{b-c}^{b+c} \frac{(b^2 + x^2 - c^2)^2 dx}{x^5} \\ &= \frac{e(1 - e') a^2}{8b} \left\{ \frac{2b(3b^2 - c^2)}{(b^2 - c^2)^2} + \frac{1}{c} \log_e \frac{b+c}{b-c} \right\} \quad \dots\dots(6). \end{aligned}$$

It will be noted from (6) that as  $c$  varies between  $+(b - a)$  and  $-(b - a)$ ,  $K$  has a minimum value equal to  $e(1 - e') a^2/b^2$  when  $c = 0$ , and increases the further the inner sphere is moved from the concentric position.

Hence from (1) the heat transfer for spheres of given sizes, emissivities and temperatures, is greatest in the concentric position. It must be remembered of course that this has only been proved for the case where the outer sphere has a poor enough internal surface reflecting power for radiation suffering more than one reflection at it to be neglected.

If  $b = 2a$ ,  $e = e' = 0.75$ , it is found from (1) and (6) that when

$$c = 0, \quad H = .715 \sigma (T^4 - T'^4),$$

and when

$$c = a, \quad H = .697 \sigma (T^4 - T'^4),$$

the latter case corresponding to the geometrical arrangement in which the spheres touch one another. The difference between the two cases is therefore very small from a practical point of view.

# A METHOD OF EVALUATING THE KINEMATIC COEFFICIENTS OF LINKED SYSTEMS

BY T. SMITH, M.A., F.INST.P.

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**ABSTRACT.** The coefficients in a function representing the energy of a system, or any function having analogous properties, may be combined to form a matrix such that the matrix of the combination of any number of systems is the product of the matrices of its parts.

## § 1. THE PHYSICAL PROBLEM

THE solution of many problems in mechanics, electrodynamics, and other branches of applied physics, is greatly facilitated by the construction of a function which represents in magnitude the kinetic energy of the system concerned, or alternatively the rate at which energy is being dissipated in the system. If the system itself contains no source of energy, any access of energy represents energy lost by the external stores from which the system can draw. This correspondence may be expressed in an equation from which the entire motion of the system can be derived. The necessary condition for the application of this method is that the energy function should be known. Its construction for some elementary systems is not difficult, and the choice of variables is to some extent arbitrary. Let us suppose these are chosen to relate to the channels by which energy can be supplied to the system; for example, in an electric network the variables may define the currents travelling along the connections with the external energy supplies. Now we may build up a more complex system by using some of these connections to couple the first system to another, of which the energy function is known, leaving the remaining channels of both systems as paths along which energy may reach the compound system. Since any gain of energy by the first system through couplings with the second system involves an equal loss of energy by the latter, the energy function of the compound system is the sum of those of the two separate parts. Before we can use this sum it must be expressed as a function of those variables alone which correspond to the external connections of the compound instrument. The conditions by means of which the variables common to the two parts must be eliminated will be seen at once if we realise that the exchanges of energy between the two parts will have the minimum values consistent with the existing flow from the external sources. Mathematically this means that the superfluous variables will be eliminated by imposing the condition that the sum of the two functions is independent of small variations in any or all of these variables.

The energy function will in general be an algebraic polynomial in several

variables, and the properties of the system depend only on the values of the coefficients in this polynomial. When the solution of the dynamical equations has been obtained for a polynomial of a definite type, all particular problems for systems having energy functions of this class are solved by evaluating the coefficients alone. Very often the converse problem is of greater importance—to discover how to construct a system having given coefficients or given values for certain functions of the coefficients. The purpose of this paper is to show that the coefficients for complex systems, built by linking simpler systems together into a chain in the way described for two systems, may be found by matrix multiplication. For practical computation this form of solution has many advantages over those described in theoretical treatises—for example, treatises on electrodynamics. No more convenient form for dealing with the converse problem could be desired.

A characteristic property of the functions which greatly simplifies the problem is that the energy is expressible either exactly or with very good approximation by a quadratic function of the variables. We will assume in the first place that only second order terms exist, and discuss the more general case afterwards. The coefficients are not necessarily numerical constants: in many electrical problems they involve operators, and the following treatment is arranged to apply when the coefficients are of this kind.

## § 2. THE MATHEMATICAL PROBLEM

The essential mathematical problem is as follows. Let  $\alpha, \beta, \gamma, \delta \dots \zeta, \eta$  each denote a set of variables and  $\mathcal{A}(\alpha, \beta), \mathcal{B}(\beta, \gamma), \mathcal{C}(\gamma, \delta) \dots \mathcal{Z}(\zeta, \eta)$  symmetrical bilinear functions of the sets of variables indicated. When all the variables of sets  $\beta, \gamma, \delta \dots \zeta$  are given the values which make the sum

$$\mathcal{A} + \mathcal{B} + \mathcal{C} + \dots + \mathcal{Z}$$

stationary, it may be expressed as a function of the variables of sets  $\alpha$  and  $\eta$  alone. A method of finding the coefficients of this function is to be obtained.

Let us write  $\alpha$  for the single row matrix of the first set of variables, arranged in a definite order, and  $\alpha'$  for the conjugate matrix consisting of the same variables arranged in a single column. Similarly let  $(\alpha\beta)$  be the single row matrix formed by set  $\alpha$  followed by set  $\beta$ , and  $\begin{pmatrix} \alpha' \\ \beta' \end{pmatrix}$  its conjugate. We may then write without loss of generality

$$\mathcal{A} = (\alpha\beta) m_1 \begin{pmatrix} \alpha' \\ \beta' \end{pmatrix} \dots\dots 2 \cdot \text{I},$$

where  $m_1$  is a symmetrical square matrix of degree equal to the number of variables in sets  $\alpha$  and  $\beta$  together, say  $n$ . The total number of elements in the matrix is  $n^2$ , of which  $n$  are in the principal diagonal. The remainder are equal in pairs, and the number of degrees of freedom in the matrix is thus

$$\frac{1}{2}(n^2 - n) + n = \frac{1}{2}(n^2 + n) \dots\dots 2 \cdot \text{II}.$$

Any matrix which is to represent this system must have the same number of degrees of freedom.



We may replace  $m_1$  by

$$\begin{pmatrix} u_1 & w_1' \\ w_1 & v_1 \end{pmatrix} \quad \dots\dots 2 \cdot 12,$$

where  $u_1$  and  $v_1$  are symmetric square matrices of degrees equal to the number of variables in systems  $\alpha$  and  $\beta$  respectively, and  $w_1$  is a general matrix, in general not square, and  $w_1'$  its conjugate. Equation 2.1 may now be written

$$\mathcal{A} = \alpha u_1 \alpha' + \alpha w_1' \beta' + \beta w_1 \alpha' + \beta v_1 \beta' \quad \dots\dots 2 \cdot 13.$$

Considering now the combination of two systems, we have

$$\begin{aligned} \mathcal{A} + \mathcal{B} = & \alpha u_1 \alpha' + \alpha w_1' \beta' + \beta w_1 \alpha' + \beta v_1 \beta' \\ & + \beta u_2 \beta' + \beta w_2' \gamma' + \gamma w_2 \beta' + \gamma v_2 \gamma' \end{aligned} \quad \dots\dots 2 \cdot 2,$$

and  $\beta$  and  $\beta'$  are to be eliminated in virtue of

$$\begin{aligned} & \alpha w_1' x' + \beta v_1 x' + \beta u_2 x' + \gamma w_2 x' \\ & + \alpha w_1 \alpha' + \alpha v_1 \beta' + \alpha u_2 \beta' + \alpha w_2' \gamma' = 0 \end{aligned} \quad \dots\dots 2 \cdot 21,$$

where  $x$  is an arbitrary linear matrix having the same number of elements as there are variables in  $\beta$ , and  $x'$  is the conjugate of  $x$ . By putting  $\beta$  for  $x$  we see that the stationary value of  $\mathcal{A} + \mathcal{B}$ , which we will denote by  $[\mathcal{A} + \mathcal{B}]$ , is given by

$$\begin{aligned} [\mathcal{A} + \mathcal{B}] = & \alpha u_1 \alpha' + \frac{1}{2} \alpha w_1' \beta' + \frac{1}{2} \beta w_1 \alpha' \\ & + \frac{1}{2} \beta w_2' \gamma' + \frac{1}{2} \gamma w_2 \beta' + \gamma v_2 \gamma' \end{aligned} \quad \dots\dots 2 \cdot 22.$$

The usual method of eliminating  $\beta$  and  $\beta'$  between 2.21 and 2.22 involves finding the conjugate reciprocal of  $v_1 + u_2$ , thence obtaining  $\beta$  and  $\beta'$  explicitly from 2.21, and substituting these values in 2.22. The process is evidently laborious, and it is an essential part of our aim to avoid it.

We first observe that the systems for which the matrices  $w$  are not square may be regarded as simplifications of systems in which they are square, the reduction in the variables being brought about by assuming the existence of linear relations between variables in the symmetrical case—very frequently pairs of variables are made equal to one another and are thenceforth represented by a single variable. As the method to be employed requires  $w$  to be square, we shall suppose that those simplifications are made after the calculation is completed or alternatively that  $w$  is augmented, in a manner consistent with the conditions of the problem, to render the matrix square. All the matrices represented by  $u$ ,  $v$ ,  $w$  are now square and of the same order, say  $n$ . The number of degrees of freedom of the system is obtained by writing  $2n$  for  $n$  in 2.11, i.e. it is  $2n^2 + n$ .

### § 3. DEVELOPMENT OF A STABLE TYPE OF MATRIX

We require, then, to construct a square matrix of degree  $2n$ , of stable type, which has  $2n^2 + n$  degrees of freedom. By stability is meant that the identities between the elements in the product of two such matrices shall correspond exactly to those of their factors. When this is the case the product of any number of matrices of this class will obviously itself be a member of the class, and it is unnecessary to consider more than two factors to establish the general laws.

Let  $p, q, r, s$  denote square matrices of degree  $n$ , in terms of which the following matrices of degree  $2n$  are defined:

$$\begin{aligned} A &= \begin{pmatrix} \dot{p}_1 & s_1 \\ r_1 & q_1 \end{pmatrix}, & A^* &= \begin{pmatrix} q_1' & -s_1' \\ -r_1' & \dot{p}_1' \end{pmatrix} \\ B &= \begin{pmatrix} \dot{p}_2 & s_2 \\ r_2 & q_2 \end{pmatrix}, & B^* &= \begin{pmatrix} q_2' & -s_2' \\ -r_2' & \dot{p}_2' \end{pmatrix} \\ C &= \begin{pmatrix} \dot{p}_{12} & s_{12} \\ r_{12} & q_{12} \end{pmatrix}, & C^* &= \begin{pmatrix} q_{12}' & -s_{12}' \\ -r_{12}' & \dot{p}_{12}' \end{pmatrix} \quad \dots\dots 3\cdot 1, \end{aligned}$$

where the accents as usual denote conjugate (or transposed) matrices.

Now let  $AB = C \quad \dots\dots 3\cdot 2,$

so that

$$\begin{aligned} \dot{p}_{12} &= \dot{p}_1 \dot{p}_2 + s_1 r_2, \\ q_{12} &= r_1 s_2 + q_1 q_2, \\ r_{12} &= r_1 \dot{p}_2 + q_1 r_2, \\ s_{12} &= \dot{p}_1 s_2 + s_1 q_2, \end{aligned}$$

and therefore

$$\begin{aligned} \dot{p}_{12}' &= \dot{p}_2' \dot{p}_1' + r_2' s_1', \\ q_{12}' &= s_2' r_1' + q_2' q_1', \\ r_{12}' &= \dot{p}_2' r_1' + r_2' q_1', \\ s_{12}' &= s_2' \dot{p}_1' + q_2' s_1'. \end{aligned}$$

The last four equations are the conditions that

$$C^* = B^* A^* \quad \dots\dots 3\cdot 21.$$

If then  $A$  and  $A^*$  are conjugate reciprocals, and similarly  $B$  and  $B^*$  are conjugate reciprocals, equations 3·2 and 3·21 show that  $C$  and  $C^*$  stand to one another in the same relation. In other words; the properties

$$AA^* = A^*A = I \quad \dots\dots 3\cdot 3$$

are stable. The conditions implied by this relation may be expressed either as

$$\left. \begin{aligned} \dot{p}q' - sr' &= I \\ -rs' + qp' &= I \\ \dot{p}s' - sp' &= 0 \\ rq' - qr' &= 0 \end{aligned} \right\} \quad \dots\dots 3\cdot 31,$$

or

$$\left. \begin{aligned} q'p - s'r &= I \\ -r's + p'q &= I \\ q's - s'q &= 0 \\ r'p - p'r &= 0 \end{aligned} \right\} \quad \dots\dots 3\cdot 32.$$

If any one of the matrices  $p, q, r, s$  is non-singular—we shall assume it is  $r$ —the one set is easily derived from the other. The first two equations of each set are conjugate. The last equations of each set state that  $r'p$  and  $qr'$  are symmetrical matrices. We may therefore write

$$p = ur, \quad q = rv \quad \dots\dots 3\cdot 4,$$

where  $u$  and  $v$  are each symmetrical, so that  $p' = r'u$ ,  $q' = vr'$ . The first relation then gives

$$urvr' - sr' = 1,$$

or

$$urv - s = R' \quad \dots\dots 3\cdot 41,$$

where  $R'$  is the conjugate reciprocal of  $r'$ . The degrees of freedom of the system are therefore determined by those of  $r$ ,  $u$ ,  $v$ , i.e. the number is

$$n^2 + \frac{1}{2}(n^2 + n) + \frac{1}{2}(n^2 + n) = 2n^2 + n,$$

which is the number needed in the matrix we are seeking.

If we substitute for  $p$ ,  $q$  and  $s$  from 3·3 and 3·31, we immediately find from the multiplication law

$$r_{12} = r_1 v_1 r_2 + r_1 u_2 r_2 \quad \dots\dots 3\cdot 5,$$

or

$$v_1 + u_2 = R_1 r_{12} R_2 \quad \dots\dots 3\cdot 51,$$

$$u_{12} = u_1 - R_1' r_2 R_{12} \quad \dots\dots 3\cdot 52,$$

$$v_{12} = v_2 - R_{12}' r_1 R_2' \quad \dots\dots 3\cdot 53.$$

Since  $v_1$  and  $u_2$  are symmetric, 3·51 gives

$$R_1 r_{12} R_2 = R_2' r_{12}' R_1' \quad \dots\dots 3\cdot 6.$$

Multiplying before by  $R_{12}' r_2'$  and behind by  $r_2 R_{12}$  we obtain

$$R_{12}' r_2' R_1 = R_1' r_2 R_{12},$$

and thus by 3·52  $u_{12}$  is symmetrical. Similarly  $v_{12}$  is symmetrical. The product of two matrices of the types represented by 3·1, 3·3 and 3·4 is thus in all essential respects similar to its factors.

#### § 4. APPLICATION

In the second section we dealt with an expression involving two symmetrical matrices  $u$  and  $v$ , and a third matrix  $w$ . In the third section we have developed a matrix definable in terms of two symmetrical matrices  $u$  and  $v$  and a third matrix  $r$ . We will identify the  $u$  and  $v$  of the one section with those of the other, and consider whether we can usefully relate the remaining matrices.

By 3·41 we may replace 2·21 by

$$\begin{aligned} \alpha w_1' x' + \beta R_1 r_{12} R_2 x' + \gamma w_2 x' \\ + \alpha w_1' \alpha' + \alpha R_2' r_{12}' R_1' \beta' + \alpha w_2' \gamma' = 0 \end{aligned} \quad \dots\dots 4\cdot 1.$$

Comparison with 2·22 suggests that we assume

$$w = -R \quad \dots\dots 4\cdot 2.$$

Making this substitution and putting

$$x = \alpha R_{12}' r_2' + \gamma R_{12} r_1,$$

so that

$$x' = r_2 R_{12} \alpha' + r_1' R_{12}' \gamma',$$

as we are entitled to do since  $x$  is arbitrary and the quantities given are of the correct dimensions, we obtain

$$2 \alpha R_1' r_2 R_{12} \alpha' - \alpha R_1' \beta' + 2 \alpha R_{12}' \gamma' - \beta R_1 \alpha' \\ - \beta R_2' \gamma' + 2 \gamma R_{12} \alpha' - \gamma R_2 \beta' + 2 \gamma R_2' r_1' R_{12}' \gamma' = 0 \quad \dots\dots 4.3.$$

It at once follows from 2.22, 3.52 and 3.53 that

$$[\mathcal{A} + \mathcal{B}] = \alpha u_{12} \alpha' - \alpha R_{12}' \gamma' - \gamma R_{12} \alpha' + \gamma v_{12} \gamma' \quad \dots\dots 4.4,$$

which corresponds exactly to 2.13 from which we started. The properties of the compound system are therefore obtainable by simply multiplying together the matrices of the type discussed in the third section. The extension to a product containing any number of factors follows immediately.

## § 5. ALTERNATIVE EXPRESSIONS

It is well known that the properties of a system may be expressed in another way closely related to that which we have adopted. For example, the variables in the electrical problem may be the values of the potential at specified points instead of currents. In the mathematical development we observe that we could have developed expressions around the matrix  $s$  instead of around  $r$ . Equations 3.31 and 3.32 show that we may put

$$q = hs, \quad p = sk \quad \dots\dots 5.1.$$

From 3.31 we also obtain

$$r = hsk - S' \quad \dots\dots 5.11,$$

corresponding to 3.41. Now let

$$\mathbf{A} + \mathcal{A} + \alpha \alpha' + b \beta' + \alpha \alpha' + \beta \beta' = 0 \quad \dots\dots 5.2$$

(this form being preferred on account of its formal symmetry), where  $\mathbf{A}$  is a function of the variables in the linear matrices  $a$  and  $b$  alone. Thus variations in  $\alpha$  and  $\beta$  make no difference to  $\mathbf{A}$ , or from 2.13, on writing  $pR$  and  $Rq$  for  $u$  and  $v$ ,

$$y \alpha' + y R' p' \alpha' - y R' \beta' + z b' - z R \alpha' + z R q \beta' \\ + \alpha y' + \alpha p R y' - \beta R y' + b z' - \alpha R' z' + \beta q' R' z' = 0 \quad \dots\dots 5.21,$$

where  $y$  and  $z$  are arbitrary linear matrices of  $n$  elements. First put  $y = \alpha$ ,  $z = \beta$ . We then derive

$$\mathbf{A} + \frac{1}{2} \alpha \alpha' + \frac{1}{2} b \beta' + \frac{1}{2} \alpha \alpha' + \frac{1}{2} \beta \beta' = 0 \quad \dots\dots 5.22.$$

Now insert in 5.21

$$y = \alpha S' q' + b S,$$

$$z = \alpha S' + b S p.$$

Remembering that

$$pR = R' p', \quad Rq = q' R',$$

and

$$h = qS = S' q', \quad k = Sp = p' S',$$

we obtain from 5.22

$$\mathbf{A} = \alpha h \alpha' + \alpha S' b' + b S \alpha' + b k b' \quad \dots\dots 5.3.$$

The matrix thus gives equally readily the coefficients of both functions.

It is worth observing that in some applications the matrices  $p$ ,  $q$ ,  $r$  and  $s$  rather than  $R$  and  $S$  and their products with  $p$  and  $q$  are the quantities known initially. In these cases the use of the matrix rather than  $\mathcal{A}$  or  $\mathbf{A}$  to represent the system is doubly advantageous. Typical examples of elementary systems are

$$p = q = \pm 1, \quad r = r', \quad s = 0,$$

and

$$p = q = \pm 1, \quad r = 0, \quad s = s'.$$

The most complex systems can be built up by combining factors of these two types alternately.

## § 6. FURTHER DEVELOPMENTS

The conclusions we have reached may be summarised by saying that the stationary values of the sums of quantities of the type

$$\mathcal{A} = (\alpha\beta) \begin{pmatrix} pR & -R' \\ -R & Rq \end{pmatrix} \begin{pmatrix} \alpha' \\ \beta' \end{pmatrix} \quad \dots\dots 6\cdot\text{I},$$

or of the associated type

$$\mathbf{A} = (ab) \begin{pmatrix} qS & S' \\ S & Sp \end{pmatrix} \begin{pmatrix} a' \\ b' \end{pmatrix} \quad \dots\dots 6\cdot\text{II},$$

where  $pR$ ,  $Rq$ ,  $qS$ ,  $Sp$  are symmetrical matrices in which the constituent elements are constants, may be obtained by multiplying the matrices

$$\begin{pmatrix} p & s \\ r & q \end{pmatrix}$$

or their conjugates

$$\begin{pmatrix} q' & -s' \\ -r' & p' \end{pmatrix}$$

in the appropriate order.  $\mathbf{A}$  may be obtained at once from  $\mathcal{A}$ , or *vice versa*, since conditions 3·31 and 3·32 show that the product of the square matrices of 6·I and 6·II is equal to 1.

We may note in passing that from the definitions, in the general case when  $r$  is not square,  $p$ ,  $q$ ,  $r$ ,  $s$  all have the same number of rows and the same number of columns, and the number of rows in one factor is equal to the number of columns in the next factor. The matrix product is therefore always determinable when its factors are given, whether the elementary matrices are square or not. To determine  $\mathcal{A}$  or  $\mathbf{A}$  the final product must be square, for otherwise  $R$  and  $S$  have not the properties needed. On physical grounds such a result is to be expected; for example, an inequality in the number of initial and final leads would make it impossible to complete all the circuits with the assumed sources of energy. The fact that the matrix product always exists may enable valuable methods of contraction to be employed. This point is probably worthy of more attention than it has yet received.

To resume however with square matrices, when the functions  $\mathcal{A}$  and  $\mathbf{A}$  are not limited to quadratic terms we may regard the elements of the constituent matrices as functions of the variables of sets  $\alpha$ ;  $\beta$  or  $a$ ,  $b$  as the case may be, instead of as constants. The theory we have so far given then yields correctly the constant terms

which represent the functions more and more closely as the variables fall in magnitude. Any additional terms which arise in the expressions  $A$  and  $\mathcal{A}$  necessarily involve differential coefficients of these functions with respect to variables of sets  $\alpha, \beta$  or  $a, b$ . Now all the terms which arise can be expressed in terms of matrices with, for example, all the members of the second set expressed either as  $\beta$  or  $\beta'$ . It follows that we may treat each matrix of variables as though it were a single variable, and differentiate with respect to it. It is advantageous to express every term in a symmetrical form. For example, in the original square matrices any element may be expressed in the form

$$e + (\alpha\beta)f' + f\left(\frac{\alpha'}{\beta'}\right) + (\alpha\beta)g\left(\frac{\alpha'}{\beta'}\right) + \dots \quad \dots\dots 6\cdot 2,$$

where  $f$  and  $f'$  are complementary linear matrices,  $g$  a square matrix, and so on. Treating every element in a similar manner, the complete matrix may be written in the symbolic form

$$E + (\alpha\beta)F' + F\left(\frac{\alpha'}{\beta'}\right) + (\alpha\beta)G\left(\frac{\alpha'}{\beta'}\right) + \dots \quad \dots\dots 6\cdot 2I,$$

the matrices composed of the variables being treated as multiplying constants. Proceeding in this way, we may express the matrix in a form analogous to a power series, the coefficients being matrices (with constant elements) increasing in degree with the power of the variable matrix.

Such a series may be differentiated and otherwise treated as an ordinary series except that the commutation of matrix factors must always be justified. The determination of the stationary value of a sum proceeds along familiar lines,\* a first approximation to the value of a variable being obtained by assuming that the elements of the square matrices are constants. The remainder of the process is equivalent to successive approximation. Thus, if we write  $\mathcal{S}$  for the sum of  $\mathcal{A}$  and  $\mathcal{B}$ , and attach a suffix to  $\mathcal{S}$  when we imply differentiation of the square matrices of  $\mathcal{A}$  and  $\mathcal{B}$  only, we have, on differentiating with respect to  $\beta$  and  $\beta'$ ,

$$(-R_1 \quad R_1q_1)\left(\frac{\alpha'}{\beta'}\right) + (p_2R_2 \quad -R_2')\left(\frac{\beta'}{\gamma'}\right) + \mathcal{S}_\beta = 0,$$

and

$$(\alpha\beta)\left(\frac{-R_1'}{R_1q_1}\right) + (\beta\gamma)\left(\frac{p_2R_2}{-R_2}\right) + \mathcal{S}_{\beta'} = 0,$$

which are transformed into

$$\begin{aligned} \beta &= \beta_0 - \mathcal{S}_\beta \cdot r_2 R_{12} r_1 \} \\ \beta' &= \beta_0' - r_2 R_{12} r_1 \mathcal{S}_\beta \} \end{aligned} \quad \dots\dots 6\cdot 3,$$

where

$$\begin{aligned} \beta_0 &= \alpha R_{12}' r_2' + \gamma R_{12} r_1 \} \\ \beta_0' &= r_2 R_{12} \alpha' + r_1' R_{12}' \gamma' \} \end{aligned} \quad \dots\dots 6\cdot 3I.$$

Substituting these values in the external factors of  $\mathcal{S}$  we obtain

$$\mathcal{S} = (\alpha\gamma)\left(\frac{p_{12}R_{12} \quad -R_{12}'}{-R_{12} \quad R_{12}q_{12}}\right)\left(\frac{\alpha'}{\gamma'}\right) + \mathcal{S}_\beta \cdot r_2 R_{12} r_1 \mathcal{S}_\beta \quad \dots\dots 6\cdot 4.$$

\* Lagrange's theorem and stationary functions. *Trans. Opt. Soc.* 27, 43 (1925-6).

The additional term on the right is of an order which justifies its neglect in proceeding to the next approximation. That is to say, we merely have to substitute  $\beta_0$  for  $\beta$  in the square matrix, or the next order terms are also obtainable by matrix multiplication.

It will be observed that equations 6.3 are of the form required to enable us to expand 6.4 by Lagrange's theorem. Every term in this expansion is obtained as a product of matrices, and the relations between all the elements correspond to those involved in matrices of the type derived in the third section. Such matrices therefore provide a means for investigating these problems, whatever the order of the functions involved may be.

## DEMONSTRATIONS AND EXHIBITS

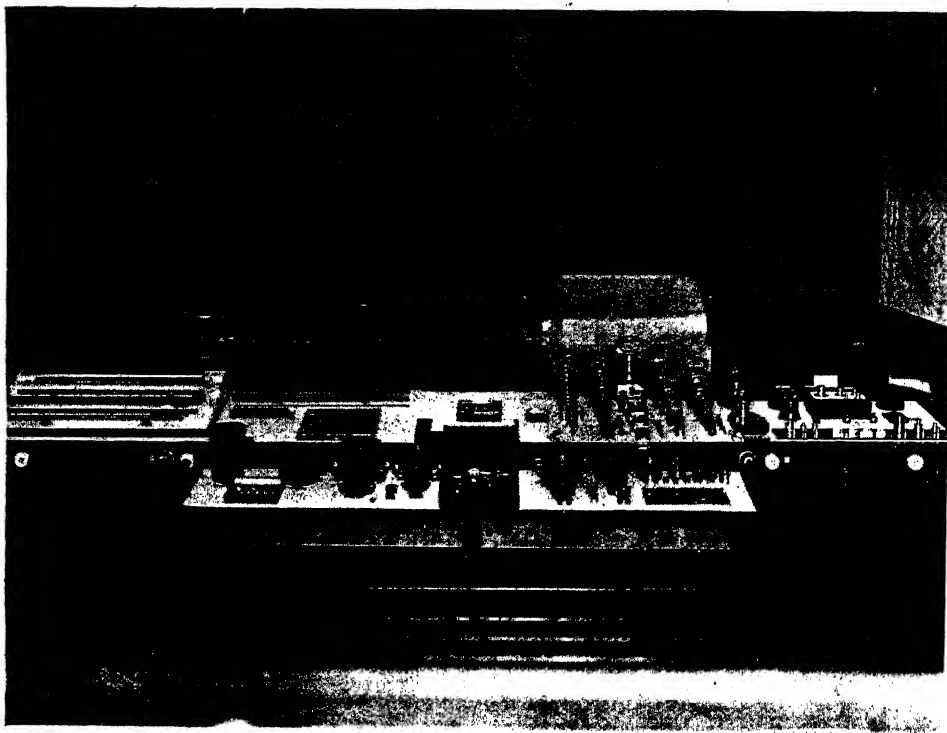
Exhibition of Standards of Length, Mass and Capacity, by J. E. SEARS, C.B.E.,  
The National Physical Laboratory.

Mr SEARS opened his demonstration by exhibiting a series of standards of length, beginning with an octagonal bronze end bar which was the standard yard of Henry VII and a square bronze end bar of Elizabeth which was the standard yard of England from 1588 to 1824. This bar, at some time in its history before it ceased to be the standard, was broken and has been roughly repaired with strips of brass and bound with wire. Even in this condition however it is only 0.01 in. shorter than the present standard yard. Following these, Mr Sears showed models of the original *Mètres des Archives*, a platinum end bar of flat rectangular section, and of the present international prototype metre—a line standard of platinum-iridium in Tresca X-form section, with the graduations on small polished areas in the exposed neutral plane of the section. Intermediate historically between these is the present British standard yard, of which a model was also shown. This is a bar of bronze (Baily's metal) 1 in. square in section, with graduations on gold plugs let into the bottom surfaces of two pits,  $\frac{1}{2}$  in. in diameter, formed in the bar at either end to half its depth. Some modern laboratory standards were then exhibited, of H-form cross-section, and made of various nickel steel alloys, ranging from invar (36 per cent. nickel) which has a coefficient of thermal expansion as low as  $1 \times 10^{-6}$  per  $1^\circ \text{C}$ . but suffers from the disadvantage of secular growth, through the alloy of 42 per cent. nickel which has a coefficient approximately equal to that of the platinum-iridium primary standard metre, and that containing 58 per cent. of nickel, which has a coefficient practically identical with ordinary steel, up to pure nickel. The three latter are all practically stable, and each alloy has its special advantages for certain purposes. Finally, Mr Sears showed some modern end standards, demonstrating how steel gauges with highly accurate surfaces would "wring" together, thus enabling a gauge of any desired length to be built up from a limited number of blocks suitably graded. He called attention to the interesting historical sequence whereby in the search for increasing accuracy the line standard had first displaced the earlier end standard, but was now in its turn likely to be beaten once more by the extremely high perfection to which modern methods enabled end bars to be finished. As an illustration he showed a yard end bar of circular cross-section made of steel with hardened ends polished flat and parallel to each other with practically optical perfection.

Passing to the subject of standards of mass, Mr Sears showed some early standards of Elizabeth (1588) including a 14 lb. weight, a nested set of flat avoirdupois weights and a nested set of cup-shaped troy weights. It is interesting to note that these are in binary multiples and submultiples of the troy ounce. The troy pound of 5760



grains was first recommended as a standard by Lord Carysfort's committee in 1758, but the Elizabethan standards were continued in use up to 1824, when the troy pound first received legal recognition. Two troy pounds constructed for the Carysfort committee in 1758 and by Kater in 1824 were exhibited. The troy pound had a short life as a standard, as it ceased to be a legal unit with the passing of the Act of 1878; the troy series from this date was again limited to multiples and sub-multiples of the troy ounce, but now on a decimal basis.



Standards of Length, Mass and Capacity.

The present standard pound is of platinum and dates from 1844, though it first received legal sanction as the standard in 1856. A model of this standard and a copy of the 1824 pound were exhibited together with a model of the more recent international prototype kilogramme—a plain cylindrical weight of platinum-iridium.

For laboratory standards such weights are of course prohibitively expensive, and it is very desirable to find some other suitable material of construction for laboratory reference standards. Brass weights are liable to oxidation. Gilt weights tarnish, and unless they are very carefully treated other surface changes appear to take place. Many materials are more or less hygroscopic, and vary in weight according to atmospheric conditions. Rock crystal, very permanent in itself, is unfortunately low in density and, moreover, is liable to surface electrification which is extremely

difficult to discharge. Experiments have been made at the National Physical Laboratory with platinised Tobin bronze, with stellite, and with nickel-chromium (80 per cent. nickel). Sets of weights in these materials were exhibited. All are better than the usual forms of laboratory weights, but the last named show the greatest stability of mass, of the order of 1 part in  $10^7$  over several years. The stellite weights are about equally stable, and are slightly harder and more resistant to wear. On the other hand, they are slightly magnetic, and much more difficult to produce than the nickel-chromium weights, as it is very difficult to get perfectly sound castings and the material cannot be machined, so that the whole weight has to be formed by grinding.

Mr Sears next exhibited the standard coin and remedy weights used for the annual trials of the Pyx, and finally a number of sets of standard weights as used by the Board of Trade and by inspectors of weights and measures, calling attention to the distinctive forms employed for different kinds of weights, e.g. avoirdupois (spherical and bell-shaped), avoirdupois decimal (octagonal), troy (smooth cylindrical with knob), metric (shouldered cylindrical with knob) and so on.

Turning lastly to measures of capacity, Mr Sears exhibited first an ancient gallon measure of Henry VII (1495) and then the "wine" gallon of Queen Anne (1707). It is interesting to note that the present Imperial standard gallon derives from the old Winchester corn gallon of  $272\frac{1}{4}$  in.<sup>3</sup> capacity, while the United States gallon derives from the wine gallon, taken over by the pilgrim fathers, which was only 231 in.<sup>3</sup>, a circumstance which is at times not without advantage to American trades. The present Imperial standard gallon, also exhibited, dates from 1824, and was originally verified by Captain Kater. It is one of a very beautiful set of measures. It is, however, only the practical realisation of the legal unit of capacity which is actually defined, on a purely theoretical basis, as the volume occupied by 10 imperial pounds weight of distilled water weighed in air against brass weights at 62° F., and with the barometer at 30 in. of mercury.

In conclusion Mr Sears showed a number of typical sets of standard measures of capacity as used by the Board of Trade and by inspectors of weights and measures: these included small metal apothecaries' measures, and also subdivided glass measures and pipettes. He apologised for the absence of a set of metric measures, and regretted that owing to their bulk he was also unable to show measures of the larger capacities—peck, half-bushel and bushel.

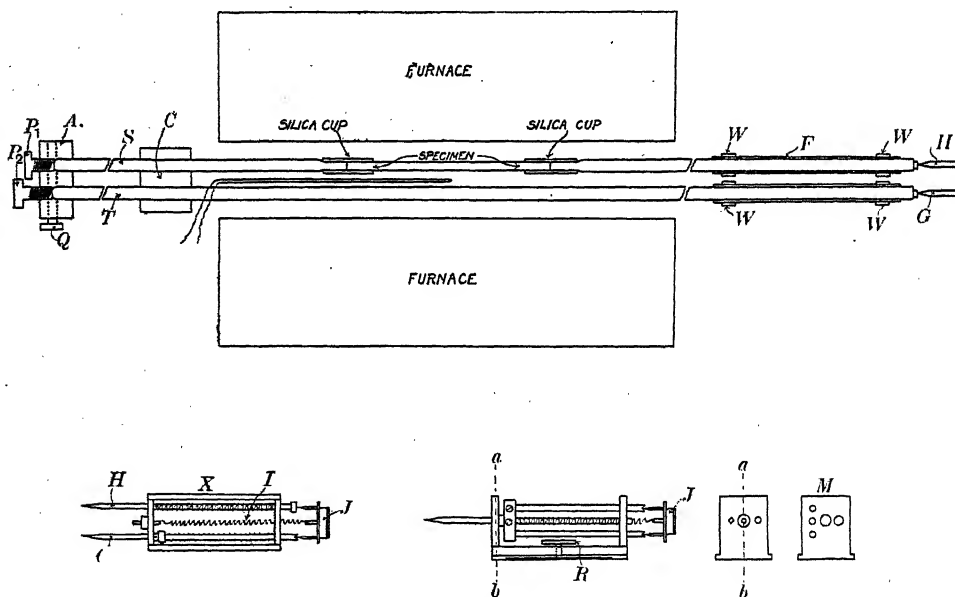
Demonstration of the Flutter of Model Aeroplane Wings, by W. J. DUNCAN, B.Sc., A.M.I.Mech.E., The National Physical Laboratory.

In recent years several instances of "flutter" of the wings or tails of aeroplanes have occurred. This flutter is an unstable oscillation which as a rule only appears at high speeds and may cause structural failures. In the demonstration, instabilities of wings possessing one, two and three degrees of freedom were exhibited. A model monoplane was shown which exhibited tail flutter, followed by wing flutter at a slightly higher speed. Another model showed that flutter occurred when the fuselage

was constrained and disappeared when the fuselage was given freedom in roll. In the cure or prevention of flutter, the principle adopted is to render the oscillations in the several degrees of freedom independent as far as possible. A model was shown which demonstrated that independence of the flexural and torsional oscillations of a wing could be secured by appropriate mass distribution. A brief description of the basis of the theory followed the demonstration.

Exhibition of an Apparatus for Measuring the Thermal Expansion of Glass from Room Temperature to the Softening Point, by FRANCIS WINKS, M.Sc.Tech.

The apparatus, which was devised by Prof. W. E. S. Turner and Mr Winks, is based on a well-known differential principle. In the present case the expansion of two rods is measured as they lie parallel in an electrically-heated furnace between a fixed stop *A* and movable pivots *H*, *G*, which cause a mirror of long focus to tilt



Apparatus for measuring the thermal expansion of glass.

by the differential expansion of the two rods. One of the rods is wholly of fused transparent silica, the other a composite rod made up of two long end pieces of fused transparent silica, together with the specimen of glass in rod form 10 cm. long, which is fixed between the two silica end pieces and carried by silica cups.

The support *A* is a fixed stop provided with two adjusting screws  $P_1$ ,  $P_2$  and a clamping screw  $Q$ . Another fixture terminates in a horizontal plate provided with a slot along which the spring apparatus *X*, which is shown in detail in the diagram, slides. When in position this latter apparatus is clamped by means of

a spring plate operated by the screw *R*. Two adjustable supports (*C* is one of them) are provided with two grooved brass plates into which fit the silica rods *S* and *T*.

The support *F* answers the same purpose, but it is longer at the top and is fitted with grooved wheels, *W*. The spring apparatus *X* consists of a brass base plate with a clamping screw and two parallel upright brass plates which are drilled and carry the pointed steel rods *G*, *H* and the mirror spring *I*. The steel-pointed rods are terminated with cups in which agates are mounted. The mirror *J* is mounted on three steel pins which fit into the agate cups and is held in position by means of the spring *I*. The furnace jacket has a water cooled pipe wound round it to prevent any radiation of heat to the base plate, on which the apparatus is mounted, although the springs *X* are so adjusted that any slight expansion of the base plate is automatically compensated. The furnace slides along the base plate and thus facilitates the adjustment of the specimens in the apparatus.

The furnace tube of silica is fitted inside with a copper lining to help maintain a constant temperature along a length of 5 inches of the furnace in which the specimens are placed.

The supporting rods *S* and *T* are of fused silica, one running the whole length of the apparatus from the fixed stop *A* until it makes contact with the steel rod *G*. The other rod is in two parts, the specimen to be tested being fitted between the two by means of fused silica tubes which slide over the ends as shown in the diagram.

Both silica rods are capped with agates at the ends which make contact with the steel-pointed rods. The latter are fitted with springs which cause the two pointed ends to be pressed up against the agate contacts. When the specimen has been fixed the furnace is made to slide into position and weights are hung over the silica rods in order to prevent the occurrence of buckling during the test. The adjusting screws  $P_1$  and  $P_2$  enable the operator to compensate for any slight variation in the length of the specimen; that is to say, the two agates which terminate the silica rods can be brought into perfect alignment before operations are commenced.

By means of suitable illumination the mirror throws an image on a graduated ground glass screen at a distance of 404 cm. The temperature of the furnace was recorded by means of a bifilar galvanometer which also works upon the same scale. In order to facilitate rapid and accurate reading over the rapid expansion range of glasses, the images are arranged to fall on the same scale in close proximity.

The specimens used are of approximately the same length (10 cm.  $\pm$  0.1 cm.) and diameter (approximately 5 mm.). The ends are ground square.

The pressure on the specimen caused by the spring contacts of the mirror apparatus is maintained constant in each test by alignment of two marks, one on the base plate and the other on the mirror apparatus. The distribution of the balance weights is also maintained constant.

The rate of heating normally adopted for rods of 5 mm. diameter is 2° per minute up to the incipient softening temperature and 1° per minute in the softening range. In cases where rods of greater diameter are used a rate of 1° per minute is adopted throughout.

Some hundreds of determinations have been made with the apparatus on glasses of widely different composition. The attached curve is for two different runs on a specimen of Chance's E.L.F. optical glass, the rods being cut from a sample of

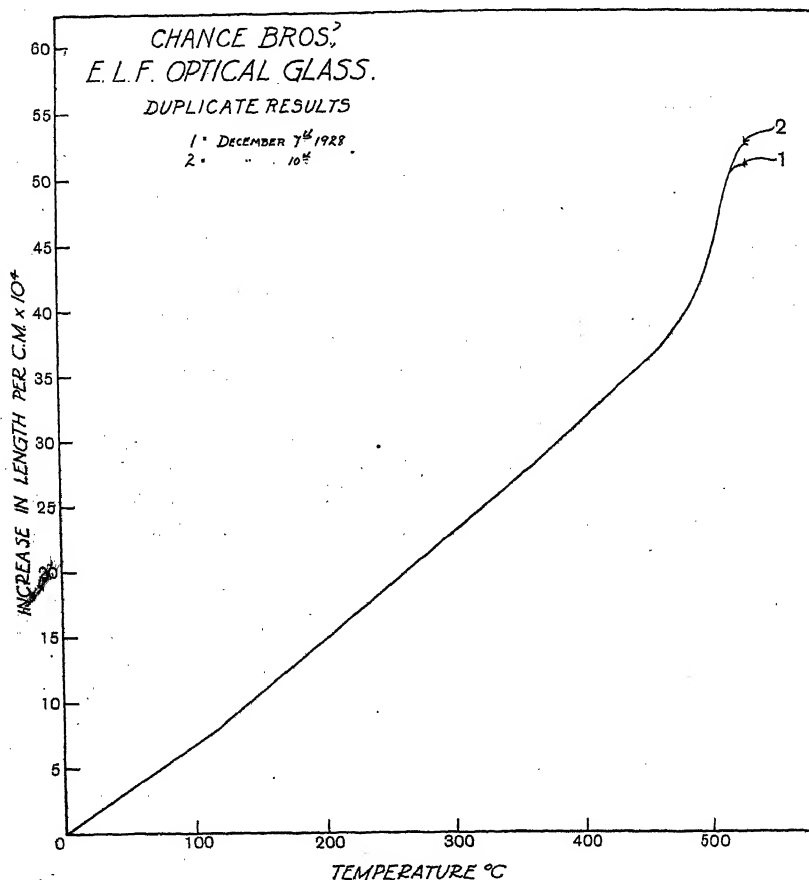


Fig. 2. The thermal expansion of Chance Bros.' E.L.F. Optical Glass.

excellent homogeneity and very well annealed. The closeness of duplication possible with samples of the same glass in the same physical condition is illustrated by the close overlap of the curves.

Exhibits relating to the Crystal Structure of Manganese and of Aluminium Alloys, by G. D. PRESTON, B.A., the National Physical Laboratory.

The exhibits represented the results of work done in collaboration with Dr MARIE L. V. GAYLER at the National Physical Laboratory.

*Manganese.* The exhibit consisted of a chart showing the arrests on the cooling curve of an ingot of manganese of 99.9 per cent. purity, with microphotographs of specimens quenched from various temperatures showing the changes of micro-

structure accompanying the phase changes in the solid state. Laue photographs of single crystals of two forms of distilled manganese were shown. These forms,  $\alpha$  and  $\beta$ , are both cubic, the former having 58 atoms associated with the body-centred unit cell and the latter 20 atoms in a cubic cell. Models of the structures derived from the results of X-ray analysis and specimens of the material used in the investigation were shown.

*Aluminium alloys.* Graphs showing the changes of physical properties which occur in some alloys of aluminium during the process of age-hardening were given. The properties dealt with included density, electrical resistivity and hardness. The changes in the X-ray spectrograms during ageing show that the changes of properties are due to distortion of the crystal lattice which accompanies the precipitation of copper from solution in the aluminium and the formation of an intermetallic compound  $\text{CuAl}_2$ .

#### REFERENCES

- Preparation of Pure Manganese. MARIE L. V. GAYLER. *Journ. Iron and Steel Institute*, **115**, 393 (1927).  
 Crystal Structure of  $\alpha$ -Manganese. BRADLEY and THEWLIS. *Proc. Roy. Soc. A*, **115** (1927).  
 PRESTON. *Phil. Mag.* **5**, 1198 (1928).  
 Crystal Structure of  $\beta$ -Manganese. PRESTON. *Phil. Mag.* **5**, 1207 (1928).  
 The Age Hardening of Some Aluminium Alloys. MARIE L. V. GAYLER and G. D. PRESTON. *Journ. Inst. of Met.* (1929).

Exhibition of some Contact Devices used in an Apparatus for the Measurement of Electrical Resistance at High Temperatures, by J. L. HAUGHTON, D.Sc., of the National Physical Laboratory.

Various methods of making contacts for electrical resistivity measurements were exhibited. The resistivity is measured by the potential drop method and contacts suitable for use in an oil bath and for higher temperatures up to  $1200^\circ \text{C}$ . were shown. For use in an oil bath, the contacts were designed mainly with a view to ease of use and accuracy of location. For higher temperatures problems connected with oxidation of the contacts, etc., come into operation, and point and knife-edge types, mounted in steatite, or in the form of rings gripping the specimen, were shown. These contacts were made of nickel or of nickel-chromium alloys. Some of the contacts are described in the *Journal of Scientific Instruments* (1929).

## PRESENTATION OF THE DUDELL MEDAL FOR 1928

TO DR C. É. GUILLAUME,

Director of the Bureau International des Poids et Mesures, Sèvres.

Dr W. H. ECCLES, President, in presenting the medal, reminded the meeting that those to whom the award is made must have "contributed to the advancement of knowledge by the invention or design of scientific instruments or by the discovery of materials used in their construction." As the inventor of invar, platinite and elinvar, and also on account of his researches upon accurate mercury-in-glass thermometry, Dr Guillaume fulfils both these conditions. Educated at the Academy, Neuchâtel, and the École Polytechnique, Zurich, he was invited to join the staff of the Bureau International as a result of his doctoral thesis on electrolytic condensers (1883). His first investigation on behalf of the Bureau related to the thermal expansion of metre-standards and was undertaken in conjunction with Dr René-Benoît. This work led him to a study of mercury-in-glass thermometry, his results being summarised in his *Traité Pratique de la Thermométrie de Précision* (1889). In 1895 he began a new determination, which occupied ten years, of the density of water. This could only be prosecuted in winter, on account of temperature requirements, and during the summer he was at this time able to search for a new material for standards of length. In 1892 he considered the suitability of nickel and its alloys, and in 1896 he studied a bar of 30 per cent. nickel-steel submitted by the Société de Commentry-Fourchambault et Decaseville as a material for weights of precision. Upon his noticing its low coefficient of expansion, the Société made, free of cost to the Bureau, 600 different alloys, one of which, containing 36 per cent. of nickel, had a thermal expansion ten times smaller than that of iron, and was named invar. This alloy has come into general use for the purposes of surveyors' standards and the pendulum rods of clocks. In 1897 Dr Guillaume produced platinite, a nickel-iron alloy containing 44 to 48 per cent. of nickel and having the same thermal expansion as glass. It is used for the leading-in wires of electric lamps, and has resulted in an enormous economy by the prevention of fractures. In 1912 Dr Guillaume invented a further alloy, elinvar, whose elasticity is invariable with temperature. It is estimated that over five million watches per annum are fitted with balance springs made of this material. In 1913 Dr Guillaume, although retaining his Swiss nationality, was elected President of the French Physical Society. In May 1915 he succeeded Dr Benoît as the Director of the Bureau International des Poids et Mesures. In 1920 he was awarded the Nobel Prize for Physics.

In conclusion, Dr Eccles remarked that Dr Guillaume has said that "nothing is more fruitful to science than the gain of a decimal place." It is the hope of all scientific workers that Dr Guillaume may long be spared to search for the extra decimal.

Dr C. É. GUILLAUME expressed his deep gratitude to the Physical Society, and rendered homage to the memory of William Dubois Duddell. He then added some details as to his work on the nickel-steels. In 1891 the Bureau International had recently distributed among the various states standards of length made of platinum-iridium: this material was admirable for the purpose, but was far too expensive for ordinary use. Dr Guillaume therefore began a search for other suitable materials. On coming across the bar of 30 per cent. nickel-steel mentioned by the President, he estimated that it had provided him with work for ten years, but in the event he required thirty years to study all the matters arising out of its remarkable properties.

After having determined the dilatation curves of pure nickel-iron alloys, and established the fact that they dipped below  $1 \times 10^{-6}$ , he investigated the effects of the addition of manganese, carbon, chromium and copper, and of tempering, annealing, drawing, etc., particularly with the view of obtaining wires suitable for base-measurement in surveying. A good melt of invar, on being drawn, has a dilatation as low as  $-0.8 \times 10^{-6}$ ; on being heated to a suitable temperature such as  $100^{\circ}$  or  $120^{\circ}$  C. and slowly cooled during 3 or 4 months it acquires a dilatation which is practically zero and unaffected by the lapse of time. These wires have effected a saving in cost of 98 per cent., and after being used for laying out one or more bases they usually retain their original length to one part in a million. Dr Guillaume himself has made about 300,000 measurements with these wires in the course of his work.

When foreign substances are added to the nickel-iron alloys their dilatation rises progressively. Dr Guillaume noticed that the curves for the thermo-elastic coefficient closely resembled those for the dilatation: and on the addition of manganese, chromium, tungsten and carbon similarly anomalous values are obtained. These pointed to the existence of an alloy with substantially zero thermo-elastic coefficient, and alloys whose coefficient is constant throughout 150 degrees C. are now being made under the name of *elinvar* (*élasticité invariable*). They are also used for making tuning forks whose pitch is independent of temperature.

The nickel-steels as at first obtained had the important defect that they were not stable with the passage of time. In 1920, however, it was noticed that this characteristic was connected with the presence of carbon, and Dr Guillaume proceeded to establish the fact that it is due entirely to the cementite content ( $\text{Fe}_3\text{C}$ ). At present invar is being produced with a percentage of carbon as low as 0.03, and although this element cannot be entirely eliminated, it can be rendered harmless by absorption with chromium, tungsten or vanadium.

Having obtained this result, he considered that, as regards the nickel-steels, his task was accomplished.



## OBITUARY NOTICES

THOMAS HOLMES BLAKESLEY, M.A., M.INST.C.E.

THOMAS HOLMES BLAKESLEY, born in 1847, was the second son of the Very Reverend Joseph Williams Blakesley, Dean of Lincoln, a distinguished scholar and churchman of his time. Educated, 1860–1865, at the Charterhouse, in the old School in Smithfield, he obtained the Watford Prize, the Havelock Exhibition in mathematics, and an exhibition at King's College, Cambridge, when the first non-Etonians were admitted to the College. He was a College prizeman, and, in 1869, a wrangler, and took his M.A. degree in 1872.

Binding himself to Messrs Easton and Amos, the well-known engineering firm at Erith, he carried out for them as resident engineer the waterworks at Burgess Hill in Sussex. In 1873 he was appointed by Lord Kimberley, as a special irrigation officer, to make extensive surveys of ancient works of irrigation in Ceylon, and to carry out necessary restorations. His description of the ruins at Sigiri was published in the *Proceedings of the Royal Asiatic Society* in 1875. Severe work and exposure to a tropical climate having affected his health, he returned to England in 1876. Practising as a consulting engineer he carried out large works at Pirmasens, in Rhenish Westphalia, for the Pirmasens Waterworks Company, and afterwards spent six months in Greece making a hydrological survey of the Plain of Attica and preparing a scheme for supplying Athens and the Piræus with water. Failure of the negotiations with the Greek Government led, however, to abandonment of the work. Consulting and parliamentary work followed.

He was elected an Associate Member of the Institution of Civil Engineers in 1873, and to full Membership in 1885. In 1885 Blakesley was appointed to a lectureship in science and mathematics at the Royal Naval College at Greenwich, a post which he held for 19 years. He became a member of the Physical Society in 1885 and was elected to the Council in 1888. He served the Society as one of its secretaries from 1890 to 1899. His term of office was marked by the first publication of *Abstracts of Physical Papers* in January 1895 under the editorship of Mr James Swinburne. He was a Vice-president of the Society from 1899 to 1904.

Blakesley's membership of the Mercers' Company of the City of London gave him opportunities for much public work. Having taken up his freedom on the attainment of his majority in 1868, he was called on the Livery in 1869 and on the Court of Assistants in 1897. He was Master of the Company 1902–3. The Mercers' Company contributed largely to the foundation and endowment of the City and Guilds Central Institution and the Finsbury Technical College; and, as representing his Company, Blakesley was a member of the General Governing Body and of the Council of those Institutions. He took an active interest in the



THE LATE THOMAS BLAKESLEY



initiation of that scheme, especially in the arrangements for teaching optics, his own favourite subject, in the Finsbury College. He was a Governor of St Paul's School from 1898 to 1903, acting as Chairman of the Board during his term of Mastership, and was admitted a Governor again in 1916. A member of the Gresham Committee, which manages the Royal Exchange and Gresham College, he was Chairman of the Mercers' side 1902-3, and was elected again to the Committee in 1917. He became a trustee of the Company's prison charities in 1925. Until his death in 1929 he continued to serve on all these bodies. He was a member of the Savile and Athenæum Clubs.

Blakesley died on 13th February, 1929, Mrs Blakesley having pre-deceased him by some years. They left no children.

The great variety of subjects dealt with in the papers and diaries exhibit the working of a cultivated, ingenious, and observant mind; their treatment habits of exact reasoning. To his friends and associates his memory is one of unfailing gentleness and courtesy.

#### SUMMARY OF BLAKESLEY'S SCIENTIFIC WORK

During the years 1880-90 Blakesley was closely occupied with electrical problems. He contributed a series of articles to the *Electrician*, subsequently issued in a volume; read papers before the Physical Society and the Institution of Civil Engineers; and published a book on *Alternating Currents of Electricity*. This last dealt with the transmission of harmonic oscillations along circuits having distributed inductance and capacity, especially submarine cable and telephone circuits, and with power transmission on lines supplying transformers in series and in parallel. The book described the use of the dynamometer for measuring power and phase difference, and the change of phase, or lag, due to the hysteresis of iron cores of transformers. The point that dynamometer measurements of power are independent of the wave form excited particular interest at the time. The book was widely read. Four English editions were issued, as well as translations into French, German, and Russian.

His work on alternating currents led Blakesley to the relations between the circular and hyperbolic functions and to the geometry of logarithmic spirals. The Physical Society published his tables of the hyperbolic functions, since reproduced in other books of tables, and a mechanical integrator deriving its argument from a hyperbolic function illustrated that relation.

The "logarithmic lazytongs" and "lattices" and the "tetrachtys," followed. These moveable linkages showed many curious properties connected with intersecting families of co-original logarithmic spirals, too intricate to be described in this short notice. A paper in the *Proceedings* of 1907 was followed by another privately circulated. The use of the lazytongs to obtain the scalar roots of an equation of any degree was described in the *Philosophical Magazine* of May 1912. The complex roots seem to have been within his reach, but that problem was not attempted. A linkage which gives a series of points on a logarithmic spiral derived

from its origin, and incidentally subdivides an angle, was found to have been previously described by Sir A. B. Kempe. A linkage which Blakesley called the "bricard," after M. Raoul Bricard the French mathematician, a generalised form of a much earlier straight line linkage due to Prof. Hart, was described in a privately circulated paper. The construction of Peaucellier's linkage on a spherical surface gave a new theorem in spherical geometry. The mechanical solution of the cubic equation he effected in several ways, obtaining, however, only the scalar roots.

Blakesley found that some of the large Moorish arches of the Alhambra are composed of arcs of logarithmic spirals, the centres and generating radii of which are indicated in the ornament of the voussoirs and architraves. This observation (which seems to be correct) has not been found in the work of any modern writer. Such spirals were used in Greek architectural ornament, and their use in southern Spain may follow an old, and lost, tradition.

He made some contributions to meteorology. The "amphisbaena" is a graduated glass tube of small bore closed at one end. A column of mercury occupies the middle part of the tube, and the closed end contains air. Two observations of the length of the air column when the tube is held (i) upright, and (ii) inverted, give the barometric height independently of temperature correction. Blakesley thought it might be useful to explorers for ascertaining altitudes, since the instrument may be short, its condition is apparent from inspection, and there is little risk of losing mercury, the bore being small.

The loss of the *Titanic* led Blakesley to examine the possibility of indicating the neighbourhood of icebergs, in fog or at night, by observations of the density of the surface water with specific gravity balls, since the fresh water which spreads from a melting iceberg sensibly reduces the surface density for considerable distances. The comparison of densities of liquids by this means is very old, and Galileo used small balls of wax loaded with grains of sand. Blakesley satisfied himself that the method, while very sensitive, was practical, and designed a simple piece of apparatus in which a set of balls, of which some float and some sink, gives the salinity of the water.

The construction of the Zeppelins suggested the use of what Blakesley called air-buoys to determine directly the buoyancy of the air. An evacuated glass sphere about 200 c.c. in volume and weighing about 20 gr. is suspended from one arm of a balance and nearly counterpoised. The position of a rider on the beam, adjusted to perfect the balance, gives a direct scale of the air-buoyancy. The sensitiveness was such that the introduction of a damp cloth into the balance case depressed the air-buoy immediately.

After 1890 Blakesley took up the study of geometrical optics, and numerous essays on its problems were published or are among his private papers. Dissatisfied with the text books used at that time he proposed new definitions of the principal terms—especially of focal length—and in 1903 published a small book on the subject which is now out of print. Several elaborate pieces of optical apparatus were constructed to his designs.

W. A. P.

## CHARLES CHREE, Sc.D., LL.D., F.R.S.

(1860-1928)

CHARLES CHREE was the second son of the Rev. Charles Chree, D.D., Minister of Lintrathen in Forfarshire, a country parish a few miles from Kirriemuir—Barrie's "Thrums." He was educated at the Grammar School, Old Aberdeen, and at the University of Aberdeen where he was awarded the gold medal as the most distinguished graduate in arts of his year. Like many other Aberdeen students, he decided to complete his studies at Cambridge, but his scholarship was so wide that he had difficulty in making up his mind whether to pursue the study of mathematics and physics or to become a classical scholar. He once told the writer that what decided him was the fact that his mathematical rivals seemed less formidable than the classical ones. Amongst the latter were James Adam and Peter Giles; the former became Tutor of Emmanuel and was a learned and brilliant Greek scholar and Dr Giles is the Master of Emmanuel and a well-known authority on philology. Chree was very friendly with both. The normal academic course of study at Aberdeen University included logic, moral philosophy, natural history and English literature. Few students can ever have been awarded more academic prizes than Chree.

After gaining a mathematical scholarship at King's College, Cambridge, he rapidly came to the front as a leading mathematical physicist. Todhunter's *Statics*, which he considered a delightful book, contributed to give him a bent in this direction.

While he was an undergraduate a serious illness originating in disease of the bone and necessitating the amputation of a thumb delayed his taking his Tripos. His degree of sixth wrangler in 1883, a year before Sir William Bragg, distinguished though it was, scarcely represents his mathematical ability. He also took a first class in Part II of the Natural Sciences Tripos, taking geology in which he was well versed as a subsidiary subject. He was elected to a fellowship at King's College in 1885 and in 1890 he was re-elected to a research fellowship.

During his stay at King's, Chree wrote many papers, most of them on the somewhat abstruse subject of mathematical elasticity. Although the present writer was only two years junior to Chree, he remembers the high eulogies passed when he was an undergraduate on Chree's solutions of hitherto unsolved problems by R. R. Webb. The excellent work he did on elasticity is proved by the large number of references to him in Love's standard treatise. Chree also did original research at the Cavendish Laboratory under J. J. Thomson who had then recently been appointed professor, with Glazebrook as assistant-director and Shaw as demonstrator. Amongst others working there at this time were Albert Campbell and the late Prof. W. Cassie, well-known fellows of this Society. As research was not then much appreciated Chree had a difficult time and had to take private pupils. He

was on the short list for several professorships. He and Cassie used to tell of amusing experiences they had with electing-committees; elastic solids, however, was not a subject that appealed to these committees.

In 1893 he was elected Superintendent of Kew Observatory. It was then controlled by a Committee of the Royal Society and financially it was in a precarious position. This entailed the most rigid economy in running costs and the minimum expenditure in plant. Notwithstanding these difficulties Kew attained under his direction the leading position among the magnetic laboratories of the world. Until the National Physical Laboratory took over the work, Chree was responsible for the testing of thousands of chronometers, watches, clinical thermometers and similar instruments. Many instruments from abroad came to be tested, and Chree made it his business to ensure that his tests should discover which instrument would give the best result under all practical working conditions. The annual publication of the marks obtained by the best watches was as eagerly awaited as that of the name of the senior wrangler in the old days when the mathematical tripos was competitive.

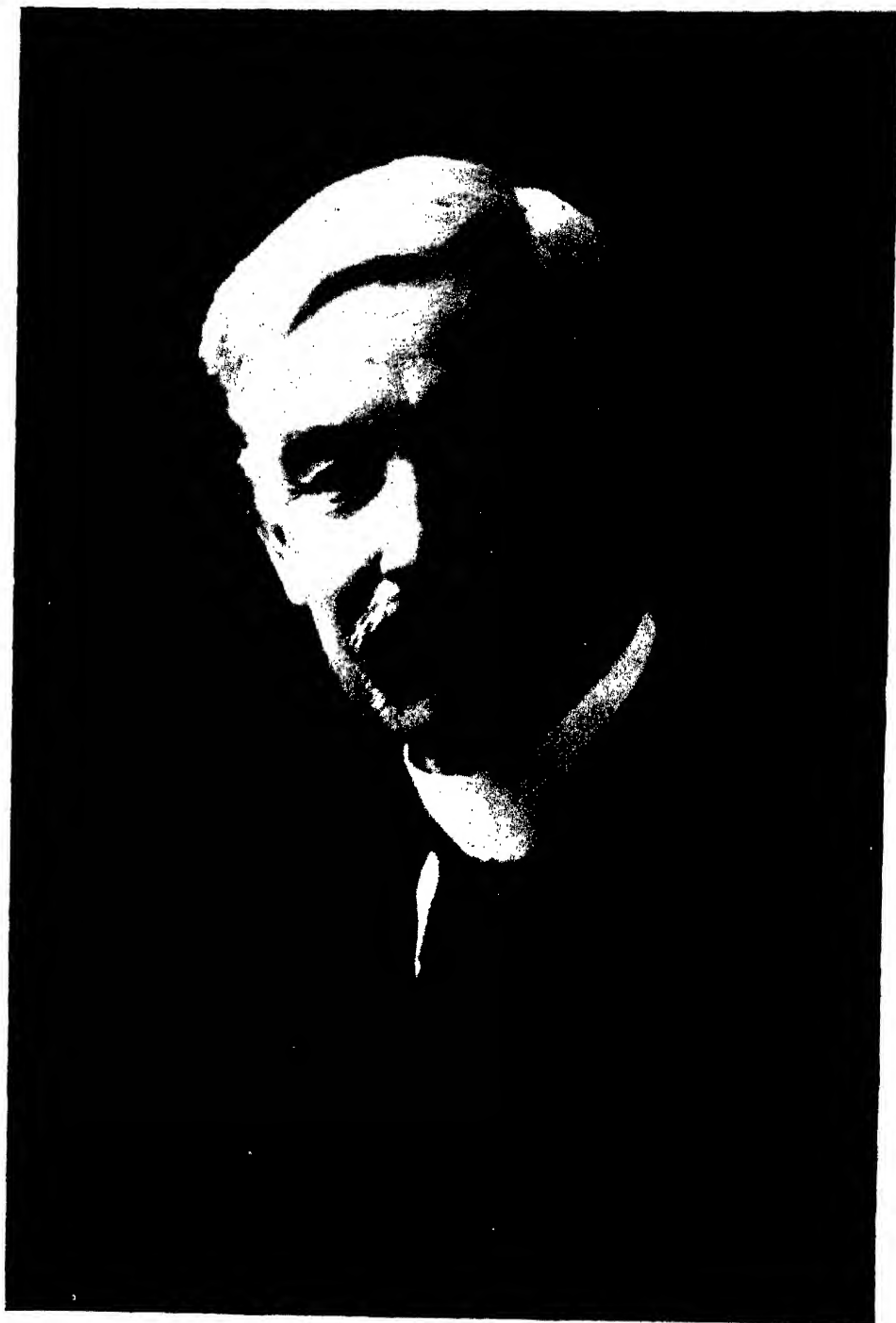
Chree was very popular with the staff at Kew. His successor Dr F. J. W. Whipple, the Assistant-Director of the Meteorological Office, and our treasurer, R. S. Whipple, were the sons of G. M. Whipple, Chree's predecessor at Kew (1878-93). R. S. Whipple was one of Chree's assistants at Kew for twelve years. Chree had always the warmest affection for old members of his staff.

He was not daunted by the vast amount of labour involved in studying records of observations extending sometimes over a hundred years. Dr Simpson\* has well said that Chree had an uncanny facility for interpreting a line of figures without plotting them on a curve and so he perhaps failed to realise that few people had this facility. Chree's work in discussing the observations made on four of the Antarctic expeditions is of great value. Two of these were under Captain Scott, including his last expedition, and one (1911-14) under Sir Douglas Mawson. The results, which represent most laborious work, are published in three large volumes. He did this work in his spare time. In addition he personally trained the magnetic observers for three of these expeditions. He fully appreciated that many of these observations were taken under great difficulties and in most unpleasant circumstances, and so desired to make the fullest use of them.

He wrote nearly a hundred papers on subjects connected with terrestrial magnetism and atmospheric electricity. During recent years he was President of the Section, dealing with these subjects, of the International Commission for Geodesy and Geophysics.

In his Presidential address to the Physical Society on February 14, 1908, Chree surprised us by saying that the formulation of theories on matters of public interest by eminent physicists was of great practical utility. He was most careful himself, however, even in making hypotheses, and always clearly pointed out the limitations of so-called general laws. This was probably due to the philosophical training he had at Aberdeen.

\* *Proc. Roy. Soc.* 122 A, 790 (1929).



*Elliott and Fry, Ltd.*

THE LATE DR CHARLES CHREE





In conjunction with the late Captain Sankey, Chree contributed a paper on the "Whirling of Shafts" to the Institution of Civil Engineers\*. For this he was awarded a Watt Medal. He was a President of the Royal Meteorological Society and took the keenest interest in its proceedings. In 1895 he received the Sc.D. degree from Cambridge, and in 1898 he was awarded the Hon. LL.D. of Aberdeen. He also received the Hughes Medal from the Royal Society.

Chree had a voluminous correspondence with scientists and enquirers from all over the world. He was very punctilious in replying to them and in this way made many friends. He often contributed to *Nature* and enjoyed continuing, by private correspondence, the discussions which he had started in its columns.

When an undergraduate at Cambridge he read the proofs and verified the examples in Frost's *Solid Geometry*. P. Frost was his tutor at King's. He always spoke of him with affectionate admiration. He also read some of the proofs of the third edition of Maxwell's *Electricity and Magnetism*, which was edited by J. J. Thomson. He was one of the few wranglers who did not go to Routh, his private tutor being Welsh of Jesus.

When he became a fellow of King's he used to invite his friends to play tennis with him in the beautiful gardens of King's College. They also had a standing invitation to his rooms every Sunday evening.

Chree was never married, his sister presiding over his house at Richmond and his brother, Dr William Chree, K.C., a well-known member of the Scottish bar, accompanying them on their golfing and trout-fishing holiday tours. When the last summons came early in 1928, Chree was in full bodily and mental vigour, and after finishing as far as possible the work on which he was engaged he most bravely and patiently waited for the end, which came on August 12. The writer saw him a few days before his death when he discussed cheerfully the work on which he had been engaged.

Chree's papers form a lasting monument to his ability and his unselfish labours for the advancement of natural knowledge. Horace, when referring to his life's work, said:

Non omnis moriar multaque pars mei  
Vitat Libitinam:...

Chree could have said the same thing. We hope his memory will long be kept green in this Society in which he always took the greatest interest.

A.R.

\* *Proc. Inst. C. En.* 62 (1905). See also *Phil. Mag.* 7 (1904).

## REVIEWS OF BOOKS

*The Earth: Its Origin, History and Physical Constitution*, by HAROLD JEFFREYS, M.A., D.Sc., F.R.S. Royal 8vo. Pp. xii + 346. (Second edition. Camb. Univ. Press, 1929.) 20s. nett.

That a second edition of Dr Jeffreys' book should be necessary within five years of the appearance of the first is a convincing proof of the high estimation in which it is held by students of earth structure. The new edition contains about 70 pages more than the old and the matter has to a considerable extent been rearranged. Seismology is treated at an earlier stage and much more fully, and a chapter on the origin of surface features has been added. A new appendix on the relation of geophysics to geology deals with cases in which Dr Jeffreys' conclusions have been ignored or contested by geologists, as for example his explanation of the origin of the Pacific mountains or his proof that the forces tending to move continents are much too small to produce the drift suggested by Wegener, or his criticisms of Joly's theory of alternate fusion and solidification of deep-seated layers. The appendix dealing with the theory of Jeans that the formation of the planets took place when the sun extended to Neptune is reprinted, although Jeans has recently adopted Jeffreys' view. It may safely be predicted that further editions of this work will be required, and it is to be hoped that more space can be found in them for the physical methods which are now in use for determining geological structure within a few kilometres of the surface.

C. H. L.

*Réseau Mondial 1922. Monthly and Annual Summaries of Pressure, Temperature and Precipitation for the World.* 4to. Pp. xvi + 116. (London: H.M. Stationery Office, 1929.) 25s. nett.

The tables which constitute the bulk of this volume are compiled under the auspices of the International Meteorological Committee from the publications of the meteorological institutes throughout the world, mainly under the control of the various governments. Two representative stations are selected in each 10° square and the means for each month and for the year of the principal meteorological elements are tabulated. The stations are arranged in zones of latitude each of 10° from north to south. Further information as to winds in the tropics and ice in the N. Atlantic and the Arctic is given.

C. H. L.

*Handbuch der praktischen Optik*, by BERNHARD HALLE. Pp. 136. (Max Harrwitz, 3. Auflage. Berlin-Nikolassee.) Paper 3 mks., cloth 4.50 mks.

This little book, which is well illustrated, should prove really valuable to all whose practical or laboratory work confronts them with occasional problems in the actual cutting and shaping of glass and of crystals. Appropriate and effective processes and machines are described by a real practician, on the whole in a clear and adequate manner; the only reservation being that the author, like others with decades of accumulated practical experience, has forgotten the numerous initial difficulties of the actual technique of grinding and polishing and in consequence gives rather meagre instructions under these heads. The style of writing is apt to be a little puzzling. Thus, on page 59 there is the following definition—"A lens is centred when the axes of the two curvatures fall into one axis"; and on page 104 the "high degree of fusibility of fused quartz" is referred to.

A. E. C.

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